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THE NATURE OF CRYSTALS

BY

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Preface by Prof. J. D. Bernal, F.R.S.

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PREFACE

It might, at one time, have been claimed that we knew far more about the nature of the interior of stars than about the constitution of the substances which surround us. We can, however, now say that our knowledge of the intimate constitution of ordinary bodies is far greater than anything that is known about the distant parts of space. Astronomy has not stood still but the progress of the analysis of matter has moved far faster. What has lagged behind, however, has been the public appreciation of these discoveries. It is probably still true to say that the scientific discoveries that are most regarded by the public are those of the expanding universe and the splitting of the atom rather than the far more immediate and practical advances of the analyses of crystal structure. This little book will I think mark one step in the correcting of the disproportion.

The new methods of X-ray analysis first developed by Sir William Bragg and his son as far back as 1913, and since brought to ever-increasing perfection, have shown that the familiar world of our experience, the solid and liquid substances with which we are every moment in contact and of which our very bodies are made, owe their properties to the regular arrangements of the atoms inside them. These arrangements can be and have been already largely mapped. We can understand now for the first time why metals are bright and malleable substances, why sand and soda give us glass, why oils are greasy and water is wet. These are not tautologies. To understand these things is to know the relation between the universal properties of atoms and the particular arrangements of them which give the substances with which we are acquainted. We have known, for instance, for 150 years or more that water is made out of hydrogen and oxygen. However useful this has been to the theoretical chemist it has always seemed unsatisfactory to the schoolboy or the plain man because it did not serve in the least to explain the common properties of water, its boiling and freezing, and its power of dissolving and of insinuating itself into so many substances. The new knowledge gives the answer to these questions. The value of understanding the structure of the materials given us by nature or traditional art is that once we understand them we are able to improve on them and will in time be able to develop quite new materials with as yet unattainable properties.

The study of structures has other than utilitarian values: the crystals out of which materials are made owe their properties not only to those of the atoms out of which they are made but to their mode of arrangement. The same atoms in different arrangements yield crystals with very different properties. These arrangements are highly regular and symmetrical and afford examples of the importance of pattern in natural processes. The appreciation of pattern is in line with the whole modern tendency to consider the importance of the inter-relation of parts in the building up of organized wholes. This aspect Mr. Ward very skilfully brings out, for he is clearly aware not only of the immediate relationships of the subject but of the bearing of the ideas it contains on other aspects of science and human experience.

There is still another way in which this little book marks a new departure. The great popular interest in science which began in the seventeenth and flourished in the eighteenth century differs from that in vogue now, in that it was then as much practical as theoretical. The ladies and gentlemen of the time not only read about science but made collections and carried out experiments for themselves. Since science became professionalized there has been a tendency to consider it a mystery too high for ordinary people. Without a 100-inch telescope no one, it is felt, could for themselves check the statements of Sir Arthur Eddington or Sir James Jeans. In this more mundane study of common matter experiment is still within the reach of anyone who has the time or inclination for it. By his suggestion for such experiments Mr. Ward may help to start a new and wholesome fashion in popular scientific writing.

It is of course physically impossible to compress even all the main advances of our new knowledge of common matter into so small a scope. But enough is shown to whet the appetite of curious and practical minds and encourage them to inquire further into the significance of substances and phenomena which until now they have taken for granted.

J. D. BERNAL.

ACKNOWLEDGEMENT

I should like to acknowledge my indebtedness to Dr. A. F. Wells for the use of his drawings in this book.

A. G. W.

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THE
NATURE OF CRYSTALS

CHAPTER I

Introduction

In recent years physical research has attracted considerable attention from the general public, owing partly to a certain number of spectacular achievements and partly to the increasing extent to which its technical applications are affecting everyday life. The incursions of scientists into the fields of religion, philosophy, and sociology are a further indication of the tendency to link science and society closer together. The movement is thus seen to be proceeding from two opposite directions; the public is beginning to wish to understand the source of the somewhat mixed blessings which result from the applications of science, while the scientist is endeavouring to see what is the ultimate outcome of his work. It is evident that such a movement can be of the greatest value for the development of society, provided that both the public and the scientist are willing to co-operate.

It is unfortunate that the branches of physical science which have attracted the greatest popular attention are those in which mathematics plays an essential part. This renders any complete understanding of them beyond the grasp of all but trained mathematicians. By means of suitable simplifications, the results of this type of work can be made fairly understandable, but the actual process by which these results are obtained is obscured by the mathematical difficulties. It is of importance to realize that the average scientific worker whose daily occupation consists of carrying out experiments is nearly as badly situated, from the point of view of understanding these theories, as a member of the general public. The theories are usually worked out by mathematical physicists who never do any experimental work, and, though those who perform the experiments can use the theoretical results, they do not understand the process by which they are derived. It is, therefore, evident that there are large sections of experimental physics which can be studied without an intense mathematical training.

In this connexion it is well to distinguish two different types of mathematical theory, in which the relation between the mathematician and experimentalist is of a different nature. In the first case the experimental results can be explained by a pictorial and qualitative method. In other words it is possible to visualize what is happening to produce the observed results. Mathematics is then used to give a precise form to the explanation, and to enable quantitative results to be calculated.

The great advances in physics in the nineteenth century were made by obtaining a clear picture of what was happening and then expressing this in suitable mathematical language. We may instance Dalton's atomic theory, the kinetic theory of gases, and the theory of electromagnetism as typical of this type of theory. The development of electromagnetic theory shows the separation into the two parts most clearly, as each was largely the work of a single man. In order to explain his experiments on electricity, magnetism, and the relation between them, Faraday considered that lines of electric and magnetic force pervaded space and that it was in this space, rather than in the charged or magnetized substances, that action took place. Using these pictorial ideas, Faraday obtained not only explanations of his past results, but also suggestions of lines along which his future work might lie. Here we see the great aid given by simple ideas to the experimental worker. Maxwell gave to Faraday's ideas the necessary mathematical form, and so laid down the method by which precise calculations could be made. In order that theoretical science may progress, both these modes of thought are necessary, since, without precise calculations which are checked by experiment, there is no proof of the validity of a pictorial theory, however plausible it may be. Provided the necessity for this is realized, it is evident that an understanding of the simple visualizable ideas of the events underlying natural processes is the key to their nature.

In contrast to this type of theoretical treatment, where mathematics is used only to give precision, there are theories in which the basic ideas are unvisualizable and can only be expressed in mathematical symbols. The ideas involved must then be concerned with events which are far removed from ordinary daily life, since, were it otherwise, we should be able to form mental pictures of them. Thus the theory of relativity is concerned with the motion of the heavenly bodies, and of atoms and electrons which are travelling at incredibly high speeds. The quantum theory is concerned with the motion of very small bodies, atoms, electrons, protons, neutrons, and the interactions between them. In both cases we are moving into strange ground, where things are either millions of times larger or millions of times smaller than those with which we are familiar. Even so, the final results of these mathematical theories must be expressed in terms of quantities which can be measured, which gives the experimental worker the material for the confirmation of the mathematical work.

These mathematical theories are justly regarded as triumphs of twentieth-century physics, and so numerous attempts have been made to present them to the public. There are, however, other branches of physics in which revolutionary advances have been made. In particular, this is the case in the study of the constitution of matter. It is well known that all substances are made ultimately from atoms. The quantum theory has met with considerable success in elucidating the way these atoms are built up from electrons, protons and neutrons, and also how the atoms behave in given circumstances. The problem which remains is to see how these atoms associate together to give us the ordinary substances with which we are familiar, living or without life, natural or artificial, simple or complex. A glance around a room provides a thousand problems of the way atoms combine to give us the materials which surround us. How are the atoms arranged to give us a diamond, and why is a diamond so different from a piece of wood or a lump of charcoal? Why is the air we breathe a gas, while water is a liquid and quartz a highly infusible solid? Why does mica split into thin sheets, whereas salt occurs as little cubes? These are not remote problems far removed from everyday life, but an immediate concern of all those who look around them with an inquiring eye.

In addition to the interest of these problems it is also evident that they are of great technical importance. The strength of a steel girder depends only on the types of atom it contains and the way they are arranged. The resistance of water to a ship passing through it depends ultimately on the arrangement and behaviour of the atoms which go to make up the liquid. It is only in the last few years that the technical operations in the treatment of metals and textiles have been placed on a scientific basis, as a result of an understanding of the way these substances are built up from their constituent atoms. So in this field of science the relation of scientific research to industrial progress is clearly brought out, whereby each mutually benefits and stimulates the other.

It is true that, since all matter is built up of atoms which obey the quantum theory, the properties of matter in bulk must ultimately depend on quantum considerations. Since, however, we are dealing with the interactions between atoms rather than events within the atom, we can use a simplified form of quantum theory. It will be seen later that metals are an exception to this, and their properties can only be fully studied using quantum mechanics, but, even here, it is possible to get a general picture of the nature of metals without recourse to a mathematical theory.

Material substances are usually considered to occur in three states: solid, liquid, and gaseous.* Usually the change from one form to another takes place quite sharply at a certain temperature. It is, however, possible by a suitable manipulation of the temperature and pressure to change a liquid into a gas without any abrupt transition; but it now seems probable that, for most solids, there must be a definite melting-point no matter what the conditions are.

In the last century the main lines of the solution of the problem of the nature of gases were laid down. These apply, in particular, to gases which are at temperatures well above the range in which the liquid can exist.† The gas consists of a very large number of molecules ‡ which, in a pure gas, are all identical. These molecules have a fairly definite size and shape, and attract each other until very close together, but then, when their electron systems begin to interpenetrate, they repel each other. When not highly compressed, the distance between the molecules in the gas is large compared with their size. They are all in unceasing motion, which becomes more and more violent as the temperature is raised. The molecules collide continuously with each other and with whatever else is in contact with the gas. It is these collisions which give rise to the pressure exerted by the gas. We can see how, in one instance, this picture agrees with the familiar properties of gases. If a balloon is blown up and placed in front of a fire, the pressure in it will increase as the gas warms up, until finally the balloon bursts. Now, using our molecular picture, the heating of a gas corresponds to an increase in the violence of the motion of the molecules. This increased violence must result in more violent impacts on the inside of the balloon, causing it first to expand, and then when it has reached the limit of its strength, to burst. These ideas can be given a full mathematical form, which enables changes of pressure on changing the temperature to be calculated, but these calculations do not add to our picture of the gas.

---

* States intermediate between solids and liquids are now known and have been given the name " liquid crystals ".

† Above a certain temperature (the critical temperature) for a given substance, the gaseous form will not condense to a liquid, however greatly it is compressed.

‡ Any pure substance, when in the gaseous state, is made of molecules, which are built from a few atoms combining together, e.g. in argon there is only one atom in the molecule, in oxygen two, in water one oxygen and two hydrogen atoms.

In a liquid the attractions between the atoms or molecules of which it is composed are sufficient to hold them together, but not to render the mass of them rigid. There is still a measure of freedom in the liquid, but it is very much restricted compared with a gas. The arrangement of the molecules is somewhat irregular, this irregularity becoming greater as the liquid is heated, until finally boiling takes place and the molecules fly apart. It is evident that the problems involved in dealing with these aggregates of irregularly arranged molecules, which are so close together that they exert strong forces on each other, are very difficult. Advances are, however, now being made in this field.

It is in the study of the third state of matter, the solid state, that we have seen great advances in the present century. The most important single advance has been the utilization of the action of X-rays on crystals to discover the arrangements of atoms within the crystals. It was already known that the arrangement must be regular, but with the new method the actual positions of the atoms relative to each other could be fixed. It was soon found that many solids which hardly looked crystalline had actually a regular internal arrangement, and that the only exceptions (if we may call them solids) were the glasses. It is the exception rather than the rule for the regular internal arrangement of the solid to result in well-developed crystal faces.

From a knowledge of the arrangement in crystals, and of the attractions and repulsions between the atoms and molecules of which they are composed, it is possible to build up a full qualitative picture of the nature of crystals and hence of all solid bodies. Much of this has already received precise mathematical expression, but certain problems remain.

The development of science has depended on the combination of theoretical insight with practical skill. In such branches of physics as nuclear research,* an extensive laboratory is required, furnished with apparatus of special design. As a result, the amateur investigator is completely excluded. However, in certain branches of physics there are still interesting experiments which can be made with only very inexpensive apparatus. Crystallography offers an ideal field for study, since much can be done with a couple of test tubes, a few dishes, and a magnifying glass. For those fortunate enough to possess a microscope, there is an endless field of fascinating work, which is concerned with objects of great natural beauty. The addition of two Nicol prisms,† to enable the crystals to be studied by means of polarized light, greatly increases the scope of the work and also the beauty of the effects obtained. For a fairly small outlay, a Wollaston goniometer can be obtained which enables the angles between the faces of crystals to be measured, and this, in conjunction with the microscope, makes quite a well-equipped laboratory. In this book I have tried to indicate a few simple experiments to illustrate points and, in particular, to give a little familiarity with the various crystal shapes—cube, octahedron, &c.

* The study of atom splitting.

† Or polaroid screen microscope fittings.

For a real understanding of the way science works, this fusion of theory and experiment is essential. If this book succeeds in persuading a few to leave their arm-chairs, take up a test tube to prepare a crystal or two, and then to try and see how the shape, hardness, colour, and all the other properties depend on the internal structure, it will have achieved its purpose.

CHAPTER II

From Hooke to Haüy

> " When any saline Liquor is evaporated to a Cuticle and let cool, the Salt concretes in regular Figures; which argues, that the Particles of the Salt before they concreted, floated in the Liquor at equal distances in rank and file, and by consequence that they acted upon one another by some Power which at equal distances is equal, at unequal distances unequal. For by such a Power they will range themselves uniformly, and without it they will float irregularly, and come together as irregularly."—SIR ISAAC NEWTON, *Opticks*.

The history of crystallography is largely the history of a single idea. From the first speculations on crystals in the seventeenth century to the present day, crystallography has been concerned with determining the regularity of structure which finds expression in various forms of crystals. Until 1912 there was no direct physical evidence of this regularity, and it is a great tribute to the work of the early crystallographers that so much of their work was found useful in the application of the direct method.

Crystals which occur naturally are often objects of striking beauty and must have attracted attention from very early times. In particular, mining communities must have been very familiar with the crystals of the various minerals. These can now be seen in any mineralogical museum. One of the finest collections is in the mineral galleries of the Natural History Museum at South Kensington, which contain splendid specimens of the majority of minerals.

Crystals are formed, either artificially or in nature, in three different ways: either by allowing the molten substance to freeze, or by crystallization from solution, or by condensation of the vapour. When the first method is employed, special precautions have to be taken to prevent the growing crystals interfering with each other.

Experiment 1.—Crystals of prismatic sulphur can be prepared by melting sulphur in a clay crucible. On cooling, a crust forms on the surface. If this is pierced and the liquid poured away, the crystals growing inside are preserved from interfering with each other. When the crucible is cold the crust can be broken off and the long needle-shaped crystals examined. Care must be taken in this experiment not to overheat the sulphur as this will cause it to change to a brown viscous liquid.*

The preparation of crystals from solution is very much simpler.

Experiment 2.—The substances given below are more soluble in hot than in cold water, so it is necessary to prepare a strong solution of each of them in hot water. This is best done by warming the water in a test tube over a gas flame and adding the solid until no more will dissolve. Then the solution is poured into a dish and left to cool. In general, a crop of small crystals will be formed which can be examined with a magnifying glass. If all but a few crystals are removed from the solution and it is then left for some days, these crystals will grow. This is due to some of the solid crystallizing out as the water evaporates. These larger crystals can be examined more easily. With care crystals an inch or more in length can be grown, but these large crystals are not usually so perfect as the small ones. In the table, the shapes of the crystals are given and also references to illustrations. Common salt is

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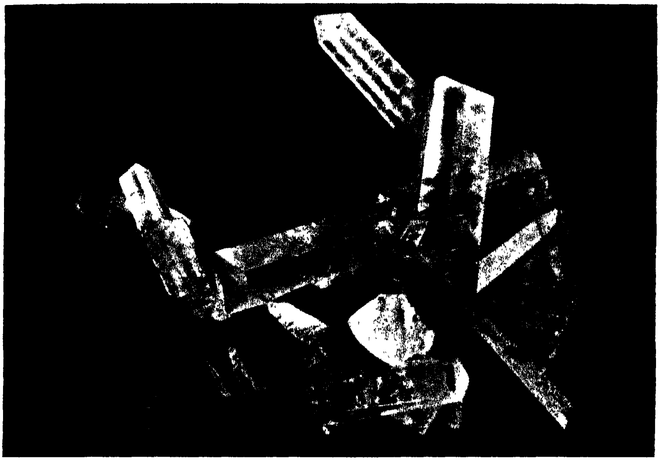
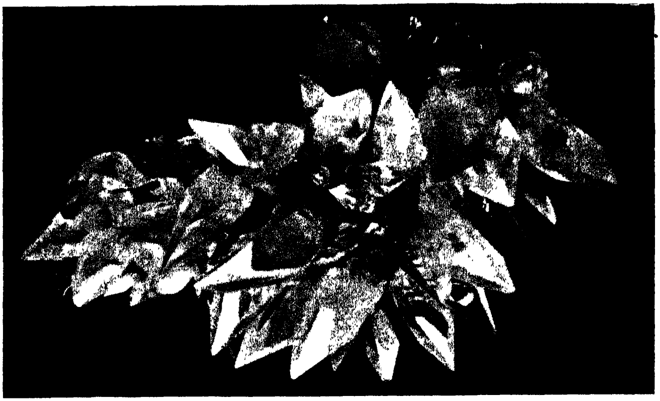
* The molten sulphur gives very unpleasant fumes, so a lid should be placed over the crucible.



(*a*) Hexagonal Prisms of Calcite terminated by Rhombohedra



(*b*) Scalenohedral Crystals of Calcite, "Dog-tooth Spar"

Crystals of Calcite from the same mine

From photographs supplied by the British Museum

only slightly more soluble in hot than cold water, so its solution has to be left to evaporate in order to obtain good crystals. Some of the commoner crystal forms are illustrated in figs. 1 to 12.

Potassium chloride (and common salt),	Cubes (fig. 1).
Alum,	Octahedra (fig. 3).
Sodium nitrate,	Rhombs (fig. 5).
Potassium dithionate,	Hexagonal prisms (fig. 7).
Sodium chlorate,	Cubes (fig. 1).

The crystals of any one substance are by no means all identical in shape. An examination of the crystals of any one of the substances mentioned in the experiment shows that some have certain faces larger than the others, while for some substances the actual faces present differ from crystal to crystal. The early workers were confronted with this problem of the multiplicity of types of crystal which correspond to a single substance. To illustrate this further, it is only necessary to look at Plate I, where there are two photographs of groups of calcite crystals. There is no apparent resemblance between the two groups, and even in a single group there are appreciable differences from crystal to crystal. Calcite is of particular importance, since its peculiar optical properties attracted much attention from Newton and Huygens in the latter half of the seventeenth century.* This naturally led to calcite being one of the first crystals to be studied thoroughly.

The first hint of a solution actually contained the key to the whole question of the structure of crystals. Hooke, who was a very able and versatile scientist, whose merits were unfortunately overshadowed by the genius of Newton, found that by piling musket shot in a regular way, he could reproduce

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* An object viewed through a rhomb of calcite appears double owing to each ray of light being split into two in passing through the calcite. This property is possessed by most other crystals to a very much less marked degree.

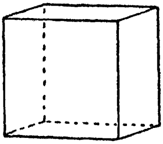

Fig. 1.—Cube

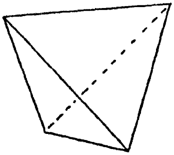

Fig. 2.—Tetrahedron

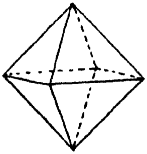

Fig. 3.—Octahedron

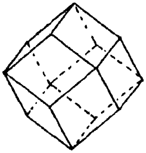

Fig. 4.—Rhombic Dodecahedron

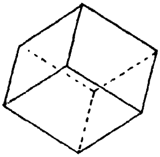

Fig. 5.—Rhomb

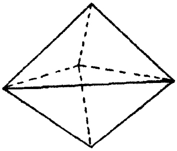

Fig. 6.—Trigonal Bipyramid

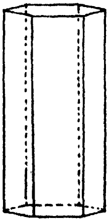

Fig. 7.—Hexagonal Prism

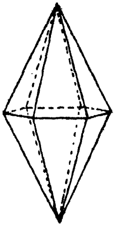

Fig. 8.—Hexagonal Bipyramid

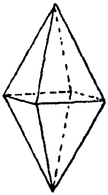

Fig. 9.—Tetragonal Bipyramid

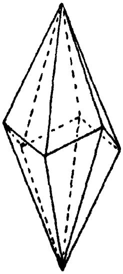

Fig. 10.—Scalenohedron

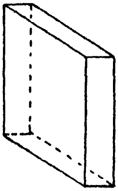

Fig. 11.—Simple Monoclinic Form

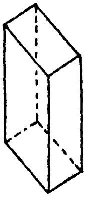

Fig. 12.—Parallelepiped, Triclinic System

all the shapes which characterize alum crystals. This conception of the internal regularity of arrangement of the particles which compose the crystal was also held by Newton. The consequences of this theory have been slowly worked out up to the present day. Plates II*a*, *b* and III*a* (p. 57) show one corner of a cube of spheres piled together and illustrate how, by removing the spheres in a regular way, we can obtain what is equivalent to a new crystal face cutting off the corner. In an actual crystal there is nothing which obviously fixes the size of this face relative to the others, except the conditions in which it is grown (p. 103). On the other hand, no matter how large this face grows, it will always make the same angle with the other faces.

It was the demonstration of this constancy of the angle between the same crystal faces, no matter how large they have grown relative to each other, which was the first triumph of experimental crystallography. Nicolaus Steno, in 1669, showed the truth of the law for quartz, and later in the century Guglielmini confirmed it for other crystals. Guglielmini also suggested that crystals were built up from small particles with plane faces, packed together, thus anticipating much of the work of the next century.

The constancy of the angles between crystal faces enables us to see the relation between the crystals in each group in Plate I. Each crystal in a group has the same faces, but developed to different sizes owing to accidents of growth. This does not, however, explain the relation between the various different faces present in the two groups, which was the next difficulty which confronted the crystallographer. Most crystals have a variety of faces, and it was essential to find the unifying principle underlying this apparent diversity. We have seen that Hooke's piles of shot could be of considerable aid in interpreting the special case of alum, but for a further advance the real need was accurate measurements of the angles between the faces for a number of crystals, rather than more speculations. The importance of identifying minerals of commercial value also stimulated this work. These measurements were made by Romé de l'Isle and his assistant Carangeot in the late eighteenth century, and their work was succeeded by the great advances made by the Abbé Haüy, who has, very justly, been called "the father of crystallography". The developments which we shall now describe are largely the results of his work.

The connexion between the two forms of calcite in Plate I is revealed by the "cleavage". If a knife edge is pressed into the edge of a crystal, a clean break usually results, giving a new face, which is as perfect as those occurring naturally. This operation is called "cleaving" a crystal, and the face formed in this way is called a "cleavage" face. Guglielmini showed that these cleavage faces obeyed the law of constancy of angle just as well as natural faces. The significance of the cleavage is, however, that no matter what the external form, crystals of the same substance always have the same cleavage directions. This shows that the internal regularity is, in each case, the same, but some accident has caused a variation in the way this is expressed in the formation of faces. All forms of calcite can be cleaved to give rhombs (fig. 5). It was very natural that Haüy should suggest that crystals are built from stacking these elementary cleavage solids together, and he showed how the various forms of, for instance, calcite could be explained on this theory. In fig. 13 the small cleavage rhombs of calcite have been stacked together to give the faces of "dog tooth spar", which is illustrated in Plate I*b*. Fig. 14 shows the shape of fig. 13 when the elementary rhombs are made smaller and smaller. The three lower faces are those of the rhombohedral ends in Plate I*a*.

In order to simplify the problem of connecting the regular packing with the faces which can be developed, we shall consider only two dimensions (i.e. what happens on a plane). We shall consider our flat crystal to be built by packing squares together—a chess-board would be a crystal containing sixty-four of these units. It is evident that the sides of the board can be faces of the crystal, but we can also obtain faces by cutting off the corners. Figs. 15, 16 and 17 show three ways of doing this. In the first case we remove just single squares in a regular way; in the second, blocks of two squares; and in the third, blocks of three squares. Now what is the relation between the three lines (or " faces " of our flat crystal) which we have generated? If the side of the small squares is *a*, then in fig. 15 we have cut off 3*a* from each of the two lines *OX* and *OY*, so the ratio of the amounts cut off (" intercepts ") is 1 : 1. On the other hand in fig. 16 we have cut off 6*a* from *OX* but still only 3*a* from *OY*, so the ratio is 2 : 1, while for fig. 17 the ratio is 3 : 1. Here is the clue to the law for which we have been searching, connecting one face with another. If we take the first face as standard, cutting off equal amounts along *OX* and *OY* to give a ratio of these

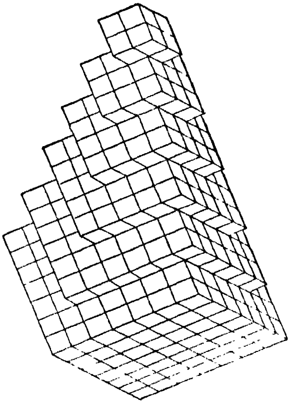

Fig. 13

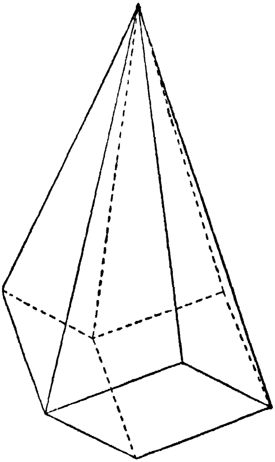

Fig. 14

From *Mineralogy*, 1902 Edition (Sir H. A. Miers), Macmillan: by permission two intercepts of 1 : 1, then all other faces must cut off intercepts in the ratio $m : n$, where m and n are both whole numbers. It is evident that, if we had built a large cube from small cubes, we should have a third intercept on the edge of the cube perpendicular to OX and OY, and that the ratio of the three intercepts would have to be $m : n : p$, where m, n and p all stand for whole numbers. We have, so far, been dealing with the special case where our elementary unit from which the crystal is built is a cube. The argument can, however, easily be extended to rectangular blocks, or to rhombs (fig. 5), or even to "parallelepipeds" (fig. 12), which are the most irregular units from which a crystal can be built.* In the case of the unit being a rectangular block of sides a, b, and c,

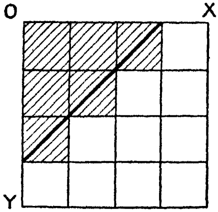

Fig. 15

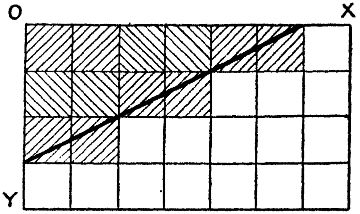

Fig. 16

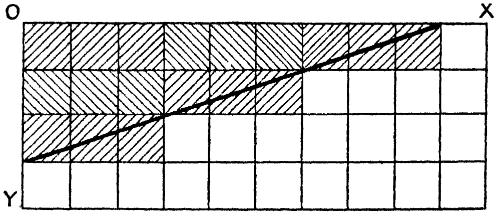

Fig. 17.—Generation of Crystal Faces

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*A parallelepiped has opposite faces parallel and looks like a match-box pushed out of shape so that there are no right angles.

an inclined face can occur which cuts off intercepts in the ratio $a : b : c$. In addition faces will be possible which cut off intercepts in the ratio $ma : nb : pc$, where m, n and p are whole numbers as before.

Experiment 3.—Draw diagrams similar to those of figs. 15, 16 and 17, only using rectangles instead of squares, of sides $\frac{1}{4}$ in. ($=a$) and $\frac{1}{2}$ in. ($=b$), and find the ratios of the intercepts.

The elementary solid from which the crystal is built is not uniquely determined, the choice being governed by convenience; so it is customary to use as edges the intersections of three actual or possible faces of the crystal. Haüy regarded cleavage as the best way of deciding what was the shape of the elementary solid, but this is by no means always convenient. It is evident that faces parallel to the sides of the elementary solid can occur in the crystal, as we saw in the case of the chess-board, but it does not necessarily follow that they will always be present.

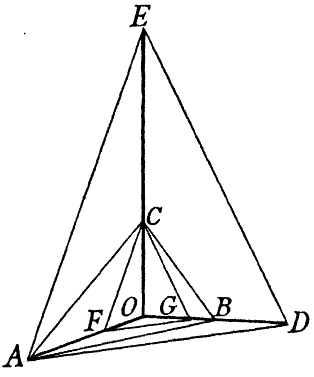

Fig. 18

Fig. 18 illustrates the procedure when we are actually dealing with crystal faces. OA, OB and OC are the directions of the intersections of three principal faces and are called the " crystal axes ". The crystal face ABC cuts off intercepts along these axes in the ratio $a : b : c$, i.e. since the scale is of no importance we can take the lengths OA, OB and OC to be a, b, and c. Then ADE is a second face of the crystal (actually we should say ADE is parallel to a second face in the crystal, it being the direction of the face which is important) and its intercepts must, we have seen, be in the ratio $ma : nb : pc$. Actually the intercepts are a, $2b$ and $3c$, so that m, n, and p are 1, 2 and 3.

We may state the law which connects together all the faces of a crystal as follows:

The ratios of the intercepts cut off from the crystal axes by any face of the crystal can be expressed as multiples of the ratios of the intercepts cut off by a standard plane.

It has become customary, since the work of Whewell and Miller, not to use this form of the relation, but to use instead an exactly equivalent one in which the amounts cut off the axes by a face have to be in the ratio $a/h : b/k : c/l$, where h, k and l are whole numbers. To do this the face ADE of fig. 18 is shifted parallel to itself to the position FGC, where its intercepts are $a/3$, $\frac{2b}{3}$ and c, giving h, k and l equal to 6, 3 and 2. These values h, k and l are called the Miller "indices" of the face.

We have seen in this chapter that the regularity of the internal structure of the crystal necessitates that the angles between corresponding faces should be constant from crystal to crystal, irrespective of their relative size or any other considerations. Then we have seen how this same regularity can give us the relation between the various different faces which occur in crystals of a single substance. Neither of these results is direct evidence of regularity, but both strongly suggest its existence.

CHAPTER III

From Bravais to Laué

> " There are many bodies, vegetable, mineral, and congealed salts, which are formed with certain regular angles and figures. Thus among flowers there are many which have their leaves disposed in ordered polygons, to the number of 3, 4, 5 or 6 sides, but not more. This well deserves to be investigated, both as to the polygonal figure and as to why it does not exceed the number 6."
>
> —Christiaan Huygens, *Treatise on Light.*

The most striking feature of a crystal is that it is bounded by plane faces, but almost equally impressive are the very symmetrical shapes in which many substances crystallize. Cubes, octahedra, prisms and pyramids are all of common occurrence in the crystalline world, and the beauty of crystals is, in no small part, due to the symmetry of these geometrical figures. It is evident that symmetry can be used as a means of classifying crystals, and also to give some information concerning the internal structure. The modern direct methods of crystal structure determination have tended to reduce the importance of symmetry to that of a convenient tool, but historically symmetry has played a very important part.

In order to describe the symmetry of a crystal, we must obtain a clear idea of the meaning of the various symmetry operations. These operations can be considered as turning one face of a crystal into another, so that, instead of having to deal with all the faces, we need only consider a few, the remainder being produced by the symmetry. Thus, wherever one cube face appears in a crystal, all six will appear, and these six faces are absolutely identical physically (though, of course, accidents of growth may result in their having different sizes). The types of operation are the following: (1) Symmetry axes of pure rotation; (2) reflection planes; (3) centres of symmetry; (4) reflection-rotation axes.

If we mount a crystal on an axis, then on turning the crystal completely around through 360°, it will be in the same position as before. But if the position of the axis is suitably chosen, it is not always necessary to turn through the full 360° before the crystal is in a position which is indistinguishable from its original one. Thus we need only rotate the hexagonal prism of fig. 19 through 60° before this occurs. At each turn of 60° the crystal is moved into a position which coincides with its original one, and since it requires six such turns to rotate the crystal completely, the axis is sixfold or hexad. If we take our axis through the centres of two opposite faces of a tetragonal prism (fig. 20), it is evident that a turn through a right angle brings the crystal into coincidence with its old position. Since four right angles make up

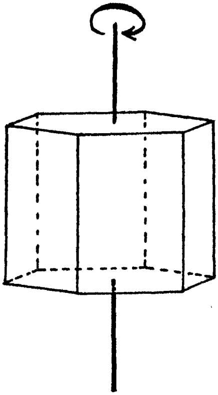

Fig. 19

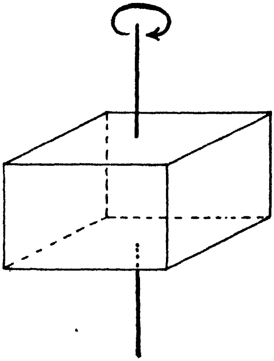

Fig. 20

a complete rotation, this axis is called fourfold or tetrad. A cube is seen to have three of these fourfold axes, each passing through the centres of a pair of opposite faces. Similarly, a threefold or triad axis requires rotation through $360^\circ/3 = 120^\circ$ before concidence, and a twofold or diad axis, $360^\circ/2 = 180^\circ$, or two right angles. We can give a general definition for a rotation axis.

A rotation axis of n- (2, 3, 4, &c.) fold symmetry brings an object into coincidence with itself after rotation about the axis through $360^\circ/n$.

This definition can be qualified in the case of crystals by the fact that only 2-, 3-, 4- and 6-fold axes occur. This is found experimentally, but, in addition, it can be demonstrated by a certain amount of straightforward trigonometry, from the law developed in the last chapter giving the relation which all faces of the crystal must obey (p. 18).

These symmetry axes are, of course, present in many of the objects which surround us, quite apart from their presence in crystals. Thus the petals of flowers are symmetrically arranged about an axis of symmetry of a degree which may take one of a large number of values.

Experiment 4.—Find the symmetry axes in the following objects. This can be done either by inspection or by turning the object about any direction which is suspected of being an axis.

1. Rectangular block, e.g. a match-box, neglecting the tray and print.	Three diad axes at right angles.
2. Rectangular table.	One diad axis.
3. Half-size biscuit tin, neglecting the difference between the lid and bottom.	One tetrad axis at right angles to the lid, two diad axes through the centres of the side faces, and two diagonally through the middles of the side edges.

The second important type of symmetry element is the reflection plane. This, as its name implies, is a plane in the object such that one half is the mirror image of the other half in this plane. These are probably even more numerous in nature than the rotation axes. Thus the middle page of this book (if we omit such details as the print!) is a reflection plane, the top half of the book being the mirror image of the lower half. This can be further illustrated by imagining the book to be cut in halves and one half placed against a mirror. Then this half and its reflection would be indistinguishable from the original book.

Experiment 5.—Find the reflection planes in the following objects:

1. Rectangular block.	Three planes at right angles.
2. Rectangular table.	Two planes at right angles whose intersection is the diad axis of Experiment 4.
3. Half-size biscuit tin.	Five planes.
4. Chair.	One plane. (We see here how a plane occurs but no axes.)

The rotation axis gives the symmetry about a line, while the reflection plane gives the symmetry about a plane. The centre of symmetry, on the other hand, gives the symmetry about a point. We can understand the nature of this symmetry operation by placing ourselves at a point which we think to be a centre of symmetry. If we now look in any direction we shall see certain objects, and, if we find on looking in the opposite direction an exactly similar set of objects, the point must be a symmetry centre. Thus the centre of the match-box is a centre of symmetry, since for every point on the match-box there is an exactly similar one on the opposite side of the centre. Of the objects we have so far considered, the match-box and biscuit tin have centres of symmetry, but the table and chair are without centres.

The last element of symmetry, the rotation-reflection axis, is of less frequent occurrence. This type of axis operates by rotating through $360°/n$, as for an ordinary axis, but then it reflects the face or object in a plane at right angles to the axis. The next rotation and reflection bring the face or line in the same side of the plane as the original one, and this process is continued until a complete rotation is completed. A calcite rhomb (fig. 5) possesses a hexagonal axis of this type, rotating through 60° and then reflecting, giving ultimately three faces on top and three below.*

Experiment 6.—Determine the symmetry of the crystals prepared in Experiment 2.

The symmetry of a crystal can be determined roughly simply by looking at it, but it must be carefully confirmed by measurements of the angles between faces. How does this symmetry depend on the underlying structure? There are thirty-two different types of crystal symmetry which are classified into seven systems. These systems have been given the following names: cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal, and rhombohedral.† Various instances of the forms of crystals belonging to these systems are shown in figs. 1 to 12. Each system includes several of the crystal classes, which represent the ways in which the symmetry elements we have described can be combined together. Any such combination must not, however, cause a departure from the law that the indices of faces must be whole numbers. Haüy's view of the crystal as built up from the piling of elementary solids would mean that the crystal as a whole would have the same symmetry as these blocks. There are seven types of block (the cube, rhomb and parallelepiped are three of these), corresponding to the seven systems, but this leaves quite unexplained the thirty-two classes which are the subdivisions of these systems.

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* The only common object with this type of symmetry is a tennis ball. If the ball is held with two of the lobes pointing upwards and two downwards the axis is vertical, and $n = 4$.

† The hexagonal and rhombohedral systems are sometimes grouped together, reducing the number to six.

Further progress had to await the development of the atomic theory by Dalton, giving the idea of groups of atoms permanently joined together to form molecules. This theory of matter being built up of these discrete groups is evidently at variance with any conception of small blocks of continuous matter. These difficulties were resolved by a succession of mathematical workers from Frankenheim in 1830 to Barlow at the end of the century. Working with three different methods, Fedorov, Schoenflies and Barlow reached the same conclusions.

This work consisted of treating the crystal as an assembly of points, which were identified by these workers either with the centres of the chemical molecule or with the centres of groups of these molecules. The first step was completed by Bravais, who showed that there are fourteen ways of arranging these centres in space so that each one is surrounded by exactly the same arrangement as the others. If we can imagine a person at one of these points, he would be unable to tell at which point he was, since the view from each would be the same. The corners of a pile of our elementary rhombs, from which we have seen so much information could be derived concerning calcite, form one such arrangement or lattice. The corners of a number of cubes stacked together form another, and similarly a pile of each of the types of block corresponding to the seven systems can be replaced by an assembly of points at the corners. It is evident that this change leaves all our argument concerning the laws of constancy of angles, and of whole number indices, quite unchanged.

In addition to the " simple lattices " which are obtained merely by replacing our blocks by points at the corners, there are lattices in which points occur, in addition, either at the centres of the blocks (body-centring) or at the centres of the faces (face-centring). Thus a cubic crystal can be based either on an assembly of points at the corners of a cube, or at the corners together with body-centring points, or at the corners together with face-centring points. Bravais showed geometrically that fourteen such arrangements of points are possible, but this still does not help us to solve the problem of the thirty-two crystal classes since the various centred lattices have the same full symmetry as the simple lattices, or our original blocks.

The unit which is repeated in order to form the lattice is not a single point but a group of points related to each other by symmetry operations. The symmetry of these arrangements limits the symmetry of the crystal as a whole. There are 230 types of arrangement, many of which, from the point of view of the external symmetry, are equivalent. So the 230 " space groups " can be classified into thirty-two classes corresponding to the thirty-two classes of symmetry of the various crystalline forms.

In the middle of the nineteenth century, Pasteur discovered a remarkable instance of the effect of the symmetry of the units of a crystal on its external form. Two of the forms in which tartaric acid is known to occur have properties suggesting that the molecules in the two forms are mirror images of each other.* Pasteur showed that the crystals of these acids were also mirror images of each other. He was able to separate the two forms of sodium ammonium tartrate, in which the molecules are also mirror images of each other, simply by hand picking the crystals according to their crystalline form. This discovery was examined on behalf of the

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* They actually rotate the plane of polarized light in opposite directions even in solution.

French Academy by the great chemist Biot, who was still devoted to science after a life-time of study. When all the experiments had been performed and Pasteur's work was completely vindicated, Biot said to him, " My dear child, I have loved science so much all my life that this makes my heart throb."

With the completion of this geometrical theory of crystals, the stage was set for a big advance. All the machinery to deal with assemblies of atoms, molecules, and groups was ready in working order, waiting for some definite information on the atomic arrangement.

This came with Laué's discovery, in collaboration with Friedrich and Knipping, of the diffraction of X-rays by crystals. X-rays are similar to light waves but have over a thousand times shorter wave-length (about 10^{-8} centimetre), which is roughly the distance between atoms in a solid. The various planes of atoms inside a crystal reflect these X-rays at certain angles between the X-ray beam and the crystal, owing to the scattering (diffraction) of the X-rays by the electrons in the atoms. The positions and intensities of these reflections give a measure of the arrangement of and distances between the atoms in the crystals. We have seen that a crystal is built up from the repetition of a unit block to form a regular pattern. It is the size of the block which governs the position of the X-ray reflections from the crystal—the smaller the block, the greater is the difference between the angles made by the X-ray beam with the crystal for which the various reflections occur.

This may be illustrated very simply for a two-dimensional pattern. If a bright source of light is looked at through a silk handkerchief (or umbrella cover, in which case a street lamp can be used as the source of light), instead of seeing the single source of light, a whole array of spots is seen, making a " diffraction pattern ". If the handkerchief is now stretched in a horizontal direction, the distance between the threads of which it is composed is increased in this direction, and shortened in the other direction. But the pattern of light spots is changed by this in exactly the opposite way, showing that the smaller the distance between the threads in the silk, the further apart the light spots are, along this direction. This is analogous to what is found in the case of X-ray diffraction from a crystal, except that in the case of the crystal we have to deal with a three-dimensional pattern.

The intensities of the various X-ray reflections from a crystal depend on the distribution of atoms inside the unit block, and can be used to find this distribution. So the measurements which have to be made in X-ray analysis are the position and intensity of the various X-ray reflections which can be obtained.

In the twenty-five years since Laué's first discovery, an exact technique has been developed to find the positions of atoms using these measurements. Sir W. H. and W. L. Bragg were pioneers in this country, and now there are hundreds of workers all over the world engaged in finding out the structures of the various types of crystals.

We shall not concern ourselves here with this technique, but rather with the results of its application. The problem with which we shall be concerned is not how the atoms are arranged, but rather, why they have the arrangement which the X-rays reveal. The second half of our task is to see how the properties of crystals such as expansion on heating, hardness, cleavage, &c., are related to the structure. It has been known since the time of Newton that these properties followed the symmetry laws which are found for the faces, but modern knowledge enables us to picture what is really going on inside the crystal.

CHAPTER IV

Atoms, Molecules and Ions

> " According to this theory, both solids and liquids consist of atoms held together entirely by chemical forces. The conception of the molecule thus almost entirely loses its significance except in the case of gases. In fact, we may well look upon any solid or liquid body as constituting a single large molecule."—IRVING LANGMUIR.

Chemistry in the nineteenth century was dominated by ideas derived from the study of the behaviour of gases. We have already seen (p. 5) that it was in this particular field that the nineteenth-century workers were peculiarly successful, and so it was only natural that the ideas developed should be applied to the solid and liquid states also. Since there was little real basis for this application, it led to many erroneous conceptions, which have only been displaced by the experimental work of the last thirty years.

All the substances in the universe are built from atoms, and, in spite of the immense diversity which these substances show, they are all built in some way or another from about ninety elementary substances, each corresponding to a different type of atom. These " elements " cannot be broken up into simpler chemical substances by any chemical means.* From the ninety elements, the remainder of the substances are built up by combining element with element to form compounds. We shall now try to see how, from our modern knowledge of the structure of the atom, we can explain the formation of links between the atoms, to make these compound substances. The structure of the atom is the subject of modern mathematical theories, but, for our purposes, we can be content with a very simple picture. This is permissible since we are only concerned with how the atoms are joined together, and not with what is happening inside them.

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* In radioactivity and the transmutation of the elements, one element does change into another, but the forces involved are far stronger than those associated with any chemical change.

The atom is fundamentally electrical in construction. It may be imagined as consisting of a very small, heavy particle, which has a positive electrical charge, and a cloud of negatively charged light particles which swarm around it. The central positively charged particle is the " nucleus " of the atom, whilst the negative particles are called " electrons ". The atom as a whole has no electrical charge, so the total charge of the cloud of electrons must be the same as that of the single heavy nucleus. Bohr's atomic theory gave to each electron in this cloud a precise path round the nucleus, rather similar to the path of a planet round the sun. The modern view of the electron does not permit us to attribute to it a definite position and velocity. It still has a definite energy, but for each state of given energy it may be found at any place in the region surrounding the nucleus, but it is much more likely to be found in the neighbourhood of the orbits of Bohr's theory. The description of the behaviour of the electron is most easily achieved by means of the theory of wave motion. In any case our description of the electrons surrounding the nucleus as a " cloud " is still valid.

The changes in the structure of the atom caused by chemical combination can never penetrate the cloud of electrons to effect any alteration in the nucleus, so all the chemical properties of the elements will depend on alterations in this cloud. The difference between the atoms of one element and another is very simply explained. It depends on the number of electrons in the cloud of each neutral atom. As we go from hydrogen, the lightest atom, to uranium, the heaviest, this number changes from one to ninety-two, and, with one or two exceptions, elements are known for all the numbers of electrons between these extremes. It sometimes happens, as we shall see later, that an electron is removed from, or added to, the electron cloud, giving the atom an electric charge. We take the number of positive charges on the nucleus as characterizing the element, since this is unaffected by any chemical changes.

The picture we have built up is that an element is made up of millions of millions of atoms, all identical,* which are constructed from a heavy nucleus, with a definite number (Z) of positive charges, and the same number (Z) of electrons circulating round it. The quantum theory has shown that there are certain rules and regulations which the electrons must obey in their motion round the nucleus. Among these may be mentioned Pauli's " Exclusion Principle ", whereby no two electrons can be in exactly the same states.† As a result the electrons are arranged in various groups which can only contain a certain limited number of electrons. These groups still retain their meaning in the newer atomic theories. The group nearest the nucleus can, at most, only contain two electrons, the next group eight, the next eighteen, and so on. Since the positive charge on the nucleus is exerting an attractive force on the electrons, it is only natural that the groups closest to the nucleus should be filled first. Thus an element with six electrons in each atom (carbon) will have two in the closest group and four in the next. As we proceed to elements for which the nucleus has a greater positive charge, the inside electrons become more and more firmly bound, so that great force has to be used to tear them away. The outside ones, however, can be disturbed more easily, and so can take part in linking atoms together. So we may formulate the rule:

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* The addition of a neutron, which has mass (i.e. substance) but no charge, to the nucleus leaves the chemical nature of the atom unchanged. Hence we call atoms with the same nuclear charge but different masses " chemically " identical.

† A state, on Bohr's theory, means a particular orbit, and an idea related to this is used to define a state in the modern theory.

In chemical changes it is only the outside electrons which are directly concerned.

The rules for finding the ways of grouping the electrons are not quite so simple as might appear from these considerations. Thus for elements for which Z is greater than 18, electrons are sometimes found in an outer group when all the inner groups are not filled (e.g. potassium). In Appendix II a table is given of all the elements. Particulars are given of the number of charges on the nucleus, and also the way the electrons are arranged in groups. The table is so constructed that, in general, elements whose atoms have the same number of electrons in the outside group fall under each other. In going from left to right we add one electron for each place moved. Hence we should expect to find a change in chemical properties as we go from element to element across the table, but that elements in each column should have similar properties, and, indeed, this is found to be true. This method of arranging the elements was discovered by Mendeléeff, and independently by Lothar Meyer, on purely chemical grounds. Its striking confirmation by modern views of atomic structure is a great tribute to the inductive method used in its discovery. The table is given in the original form discovered by Mendeléeff, and so the elements in the rows $4A$, $4B$, $5A$, &c., fall under each other. It can be seen from the electronic structures that the elements of one column in the A rows resemble each other, and similarly those in the B rows resemble each other, but there is little in common between the two groups so obtained. More recent forms of the table emphasize this by separating out the two groups. The structures are further illustrated very diagrammatically in fig. 21 for a few atoms. These diagrams are intended to emphasize the groupings rather than to give any idea of the internal constitution of the atom.

Our next task is to derive from the grouping of the electrons for the various elements, the ways in which one atom can combine with another. The first striking feature is that the elements of one column in the table will not form stable compounds with any of the other elements. This is column o, which contains helium, neon and argon. These three elements are gases at ordinary temperatures and are found in the atmosphere. Nearly 1 per cent of air is argon, and its main use is in the manufacture of gas-filled lamps. Helium is a very light gas and is used to fill airships. These uses reflect the inability of the gases to combine with other elements, since the filaments in the argon-filled lamps are not attacked by the gas, and helium does not burn, thus rendering airships filled with it safe from fire. Neon is now well known owing to its use in neon signs. The atoms of these three so-called "rare" gases attract each other so feebly that they do not liquefy until far below the freezing-point of water. The refusal of these atoms to unite with other atoms shows

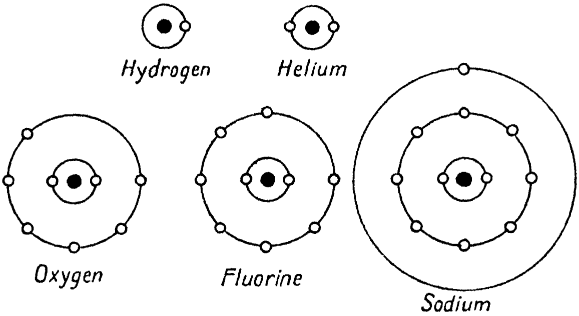

Fig. 21.—Electronic Structure of Atoms
Diagrammatical representation to illustrate the grouping of electrons

the great stability of an electronic structure with certain numbers of electrons; e.g. 2 for helium; 2, 8 for neon; 2, 8, 8 for argon. Since these groupings have such great stability it requires very little energy to add electrons to atoms with a few less electrons than these rare gas structures, or to remove electrons from atoms with an excess. In some cases there may even be a gain of energy in this process. The endeavours of the atoms to arrange that they have one of these stable configurations of electrons provide the keys to the ways in which atoms combine.

We have three main types of combination, depending on three different methods of making the number of electrons up to the stable group for the various elements. These are (1) transferring one or more electrons from an atom with an excess over the rare gas structure to one with a deficit; (2) a sharing of electrons between two atoms both of which have deficits; (3) a removing of electrons from a number of atoms all with an excess of electrons. We will consider the mechanism of these processes in more detail now, and in succeeding chapters we shall trace the consequences in the structure of the solid state.

The combination by transference of electrons is called " ionic ", and the atoms which receive charges by this transfer are called ions (positive or negative according to whether the atoms have lost or gained electrons, the electron being, of course, negatively charged). The existence of these ions was first shown in the conduction of electricity by solutions of salts. In these solutions the ions act as the carriers of electricity. We will consider as an example of an ionic solid common salt (sodium chloride), which is made by combining the element sodium * with chlorine. Sodium has (App. II)

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* Sodium is the metallic element which is present in common salt, washing soda (sodium carbonate), Chile saltpetre (sodium nitrate), and hundreds of other compounds. The metal itself is only made with difficulty and is very reactive, combining with water and air. It is kept under an oil.

2, 8, 1 electrons, which arrangement has one more than the stable group 2, 8, and chlorine has 2, 8, 7 electrons, one less than argon, 2, 8, 8. It requires a certain amount of energy to tear the electron from a sodium atom and add it to the chlorine atom, but this leaves both the atoms charged. The energy due to the attraction of these charges is much greater than that necessary to effect the transfer of an electron from one atom to another. As a result the molecule of one atom of sodium and one atom of chlorine is stable in the gaseous state, and this is actually the constitution of the vapour of common salt—a large number of molecules consisting of one ion of sodium and one of chlorine. When we cool this vapour down so that it condenses to the liquid, each negative chlorine ion tends to collect a number of positive sodium ions around itself, and each sodium ion collects chlorine ions. This is because the attractions between the ions are not confined to one direction, but depend simply on the distances between them. In solid sodium chloride (i.e. in the ordinary crystals of salt) each sodium ion has six chlorine ions round it, and similarly, each chlorine has six sodium ions as its neighbours. In molten common salt the numbers are more variable, and the number for any one ion changes from time to time, owing to the more violent motions of the ions.

As a second example of how an ionic compound is formed we may take calcium fluoride, which occurs naturally in beautiful cubic crystals as the mineral fluorspar. Calcium * has 2, 8, 8, 2 electrons and fluorine has 2, 7. Hence combination takes place by the calcium atom losing its two outer electrons, leaving it doubly positively charged, and each of two fluorine atoms gaining a single electron to make them

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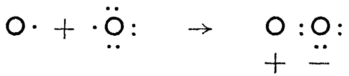
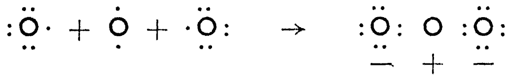
* Calcium is a metal, and occurs combined as limestone (calcium carbonate), quick lime (calcium oxide), slaked lime (calcium hydroxide). Calcite is the same chemical substance as limestone, but is, as we have seen, found in fine crystals.

each singly negatively charged. Then a neutral molecule can be formed from one calcium and two fluorine atoms. This molecule only exists in the gas, but the individual ions of calcium and fluorine exist in the liquid and solid, each surrounded by a number of ions of the opposite charge. Since each calcium ion is counterbalanced by two fluorine ions, each calcium ion has twice as many fluorine ions around it as there are calcium ions round a fluorine ion. The numbers actually found in the crystal are eight and four.

We may represent the genesis of molecules of sodium chloride and calcium fluoride diagrammatically, though, of course, the electrons in the ions cannot really be thought of as stationary or as being distributed in a plane. We omit the inner electrons which are not involved.



Sodium + chlorine → sodium chloride



Fluorine + calcium + fluorine → calcium fluoride

Almost all compounds formed by combining elements of columns (1) and (2) (App. II) with elements of (6) and (7) are of this ionic type, and in addition there are compounds involving elements of columns (3), (5) and (8).

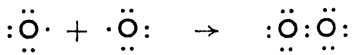
Experiment 7.—Lithium is an element similar to sodium, having an excess of one electron over the stable group 2 (helium). Show what electrons are transferred in the compounds lithium fluoride (LiF), lithium oxide (Li_2O), and lithium nitride (Li_3N), and show how the electrons are arranged in molecules of the compounds in the gaseous state.

We will now consider the nature of bonds formed by the sharing of electrons. The simplest instance of this is the combination of two hydrogen atoms to form the hydrogen molecule. Each hydrogen atom has one electron, and so it requires one more to give it a rare gas structure (helium 2). This it achieves by sharing its electron with another atom, to give a molecule in which each atom contributes one electron to form an electron pair bond. The electrons form a common electronic cloud round the two nuclei. We may represent this diagrammatically:

$$\mathrm{O}\cdot + \cdot\mathrm{O} \quad \rightarrow \quad \mathrm{O}:\mathrm{O}$$

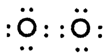
Two hydrogen atoms → the hydrogen molecule

If we have two atoms of fluorine (2, 7), it is evident that if we try and form a compound by transferring an electron, we shall leave one atom with 2, 6 electrons in giving the other its complement 2, 8. This requires so much energy that it would not give rise to a stable compound. If, instead, each atom shares one of its electrons with the other, then this effectively gives each a full complement of eight electrons. Such a compound is very stable and so we find fluorine, chlorine and bromine occur as molecules each containing two atoms linked together by sharing a pair of electrons. We can represent the combination as follows:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}: \quad \rightarrow \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:$$

Two atoms of fluorine → fluorine molecule

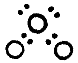


$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:$$

The oxygen molecule

In oxygen (2, 6) each atom requires two more electrons to make up the neon structure (2, 8), and so four electrons are shared between the two atoms as in the diagram, making a diatomic molecule. The energy of combination for these compounds is not, as in the ionic case, just an attraction of charges, but depends essentially on the process of sharing the two electrons. As a result, we find that when two atoms are joined to a third by these " electron pair bonds ", the electronic structure fixes the angle between the two bonds.

Thus in the molecule of water (H_2O), the angle between the bonds is, approximately, 109°.



Water molecule

Of supreme importance are the bonds of this type formed by the element carbon (diamond and graphite are forms of carbon). Carbon lacks four electrons to make up the structure 2, 8, and so the atom can form four electron pair bonds with other atoms, such as chlorine, fluorine or hydrogen which each require one more electron. These bonds are at fixed angles to each other. If the carbon atom is at the centre of a tetrahedron the four bonds are directed towards the corners, which means they are as evenly and symmetrically spaced as possible (fig. 22). Carbon atoms can link one with another to form chains, and so we obtain all the immense variety of carbon compounds.

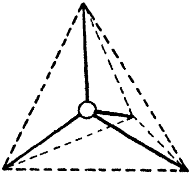


Fig. 22—Bonds of Carbon Atom

The electron pair bond is called also the homopolar (like ended) bond, in contrast to the ionic, or heteropolar, bond. Occasionally one atom supplies both the electrons to form the bond, but we shall not be greatly concerned with this case. It is also possible for atoms to share electrons so that one has more than the normal stable outside group, ten and twelve electrons being fairly frequently found to occur.

Experiment 8.—Show how the electrons are arranged in carbon tetrachloride (CCl_4), remembering that the four atoms of chlorine are distributed in space around the carbon atom. Examine also the way electrons are shared in phosphine (PH_3) and sulphuretted hydrogen (H_2S).

We have so far considered compounds formed between atoms, some of which have a deficit, and some an excess over the rare gas structures, and also between atoms all of which have a deficit. Now we require to investigate the compounds between atoms, all of which have an excess of electrons. This type of aggregate is stable only in the solid and liquid states, and is characteristic of metals. If we examine Appendix II, we shall see that all the well-known metals have a small number of electrons in the outermost group.

The excess electrons may be thought of as being freed from their atoms and are held in common by the positively charged ions which are left. The electrons serve as a sort of glue, sticking the ions together, but they are still fluid enough to move round them. The electrons belong to the aggregate of ions as a whole rather than to one or two ions in particular. Since the electrons are not compelled to remain on one atom, if we apply an electric field to the metal, the electrons can drift under the action of the field. The drift of the negatively charged electrons constitutes an electric current through the metal, and the ease with which this takes place explains the characteristic high conductivity of metals. The heat motion of the ions, together with imperfections in their arrangement owing to the presence of impurities, impede the motion of the electrons, and so give the metal a definite resistance to the passage of an electric current. The ionic and homopolar crystals have no such free electrons, and so do not conduct electricity to any appreciable extent. Salt is a bad conductor, since the charged ions can only move with great difficulty. If, however, the salt is heated, the ions move more and more freely, until finally on melting the salt becomes quite a good conductor.

We have described the three types of bond: the attraction between the charged ions which are formed by the transfer of electrons, the homopolar electron pair bond, and the metallic bond, where the free electrons bind the whole mass of positive ions together. These correspond to the three main types of force between atoms or ions: ionic, homopolar and metallic. In addition there is a fourth type of force, which is weaker than the others and is the result merely of the interaction between the motion of the electrons in separate atoms or molecules. Thus the atoms of helium, neon or argon attract each other very weakly as a result of this force, and this is the form of binding which causes these elements to liquefy and solidify. Where other types of force are present, these small forces are almost negligible, but they are nevertheless always present between any two atoms. They are of great importance between neutral molecules such as the organic carbon compounds, where the bonds inside the molecule are homopolar.

It is evident that, when solid crystals are built up from the atoms or molecules, the forces of attraction and repulsion between these atoms and molecules will decide the way in which they are arranged. So in studying solids we divide the huge number of compounds into classes, according to the types of force present. Thus we see at once we have four main classes, according to whether the forces are ionic, homopolar, metallic or the weak universal type to which the name " residual " has been given. These are not narrow classifications, for many substances lie on the border lines. It is also possible for two types of force to be present in one crystal. However, the division greatly aids us in our attempt to understand the constitution of solid substances.

CHAPTER V

Methods of Model Construction

> " There are two distinct ways of studying space—our familiar space at present in use. One is that of the analyst, who treats space relations by his algebra, and discovers marvellous relations. The other is that of the observer or mechanician, who studies the shapes of things in space directly."—C. H. HINTON.

Structural crystallography is simply the science which determines and then studies those space arrangements of atoms, ions, and molecules which are found in crystalline solids. To appreciate the achievements of this science it is not essential to be familiar with the rules of algebra; what is necessary is an ability to picture the regular patterns of atoms arranged in space. This ability is closely related to the power of an artist to visualize his work, of an engineer to see the machine or structure he is designing as a finished whole, of a surgeon to know the location of every vein, artery, and nerve in the region of the body on which he is operating. Each requires the power to visualize a considerable amount of detail, and to see the relations the various parts bear to each other in space.

In crystallography our task is considerably simplified since we have to deal only with regular arrangements. So if we can imagine the unit of the pattern, the rest can be built up merely by repetition. The artist, engineer and surgeon spend years acquiring their special abilities, but their difficulties are increased also by the very limited use they can make of models. Thus before an engineer can build a model of a machine, he must already have conceived its general form, although a model can then be used to suggest detailed modifications. The results of X-ray crystal structure analysis, however, give us all the necessary information for the construction of models, so that the training necessary to understand the nature of crystal structures need be neither long nor laborious. It is essential to realize that in order actually to find crystal structures by X-ray methods, much greater skill in handling arrangements of atoms is required; but we are concerned here with the known structures of crystals, rather than the method by which they are discovered.

We see, then, that the nature of crystals can most easily be grasped by means of models. All forms of sketches, whether plans or perspective views, are unsatisfactory until a measure of experience has been gained with models. Again the value of building a model is much greater than simply looking at one. The work of building gives an intimate appreciation of the result, which no other method can give. Methods of building models are given below, and though their construction is not essential to gain some understanding of the succeeding chapters, the reader who does build them will be rewarded with a greatly increased insight into crystalline structure, and, incidentally, will also acquire a keener conception of space relations in general.

We have seen that atoms, ions and molecules have fairly definite sizes, which result from the resistance which the electrons of one atom give to interpenetration by those of another. Naturally the size of a neutral atom is different from that of the ion of the same element, since, though the nuclear charge is the same, the number of circulating electrons is different.

Neutral atoms and the simple ions are conveniently represented by balls of a definite radius, which varies from atom to atom and from ion to ion. When considering the electron pair method of combination, it is no longer possible to talk of an atomic radius, since the electron systems of the two atoms are not entirely separate. Instead we take the distance between the nuclei, which we can regard as the centres of the atoms, as the quantity to be used, and this we term the " bond length ". If a homopolar bond is formed between like atoms, then we can regard half the bond length as a characteristic of the atom. When different atoms combine by means of a homopolar bond, the distance between the atoms is the sum of these half-bond lengths. This rule is only an approximation, but it is extremely useful. The majority of molecules (e.g. the hydrocarbons made from chains of carbon atoms) cannot be treated as spheres,* but have a very definite shape, which can be obtained, roughly, by taking spheres of appropriate radii around the nuclei of all the atoms in the molecule.

In metals the atoms act as spheres also and they have a " metallic radius ". This radius includes the free electrons, which do not occupy any space which has to be taken into account in packing these spheres together.†

There are two types of model, each useful and complementary in their functions. The first type is made by packing together balls or shapes representing molecules, which are of correct scale, until we have built the unit of the pattern (" the unit cell "). The whole crystal is then built by repeating this pattern indefinitely. This type of model is the nearest approach to an accurate picture of the inside of a crystal, but it is hard to construct in complicated structures, and also the outside balls obscure those inside. To avoid these difficulties we use another type of model in which we concentrate on the atom centres and the way they are arranged, always bearing in mind the spheres of electrons which really surround them.

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* Unless they are freely rotating in all directions.

† This convention has arisen from its great utility in experimental work. The radii of these spheres are the same for a given element, both in the pure metal and in its alloys.

METHOD 1.—Crystals made of atoms all of one size, such as pure metals, neon and argon, can easily be made using either ball-bearings, wooden balls or ping-pong balls. If the latter are used, permanent models can be constructed by gluing the balls together. It is well worth while to make a few models of this type, in particular the three characteristic metallic structures, close-packed cubic (p. 57), close-packed hexagonal (p. 57), and body-centred cubic (p. 89). If sets of balls of different sizes can be obtained, ionic crystals can be made, and, indeed, an ionic crystal for which the positive and negative ions are the same size can easily be made by colouring one set of ping-pong balls and using the plain and coloured sets as the two ions. An example of this is potassium fluoride (KF), which has the same structure as sodium chloride, but the radii of the ions are almost equal (both equal to 1·33 in units of hundred millionths of a centimetre, which we shall in future refer to as Ångström units, and symbolize as, for instance, 1·33 Å.). In every case it is only necessary to build the smallest unit of the pattern, which corresponds to the primitive block of Haüy's theory. Often the relations of the various atoms to each other are made clearer by building a little more of the structure, but the whole structure is made simply by repeating the primitive block.

METHOD 2.—For this method a wire framework has to be constructed, on which the centres of the atoms can be located. Then coloured balls of plasticine can be moulded round appropriate points, each colour corresponding to a type of atom.* The advantage of this method is that the relation of any atom to its neighbours can be seen at a glance since the whole structure is open. The danger in using this type of model is that the size of the atom tends to be forgotten.

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* For permanent models "plastone" may be used which sets hard on exposure.

The best way of making a framework is by soldering pieces of wire together. The wire requires to be stiff and straight —stout copper or brass wire is quite suitable and is easy to solder. Proficiency in soldering is fairly easily acquired, but if no soldering iron is available, the wire can be waxed together with white or sealing-wax. This is not nearly so satisfactory, since the joints are not very strong. Fig. 23 shows the framework required for one unit of a cubic crystal, and this can be used for all the cubic crystals described in this book.

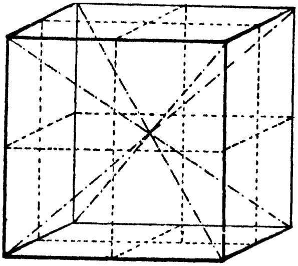

Fig. 23.—Cubic Framework

If the cube is to be 5 in. × 5 in. × 5 in., the lengths of wire required are: 24 of 5 in.; 4 (the diagonals) of $5 \times \sqrt{3} = 8\frac{3}{4}$ in., allowing a little for soldering.

Certain of the positions in the cubic framework are of great importance, since they represent the most frequent locations of the centres of the atoms. Cubic arrangements are highly symmetrical, so we find that certain of these positions are " equivalent ". This means that if an atom centre is located at one position, there must be atom centres of the same type of atom at all the other " equivalent " positions. Thus if we have an atom centre at the middle of the face of the cube (position *B*, fig. 24), there must also be atoms at the centres of the other five faces.

The symmetry of all cubic arrangements is not the same. In a crystal with full cubic symmetry, the eight positions *E* and *E′* (fig. 24), at the centres of the eight small cubes, are equivalent, but in less symmetrical crystals (e.g. diamond), the atoms are found in only four of these positions.

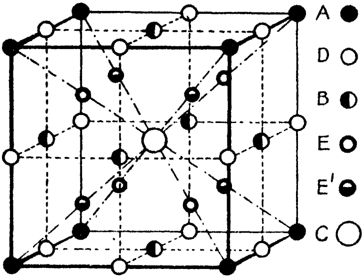

Fig. 24.—Equivalent Positions on the Cubic Framework

For convenience of reference, we shall give the various common equivalent positions on our cubic model framework. These are illustrated for the cube in fig. 24.

Position	Symbol	Number of Equivalent Positions
Corners of the cube.	A	Eight.
Centres of each face.	B	Six.
Body centre of the cube (intersection of the four diagonals).	C	One.
Centres of the edges.	D	Twelve.
One-quarter and three-quarters of the way along a diagonal, i.e. in the centre of each of the eight cubes obtained by halving all the sides.	E, E′	Eight, or in a less symmetrical arrangement, two sets of four.

Models of crystalline structures, when the lattice is no longer cubic, can be built using other frameworks. In the case of molecular crystals, the unit from which the pattern is built is the molecule rather than the separate atoms, the binding between atoms within the molecule being much stronger than that between molecules. It is, therefore, usually easier, and also clearer, to build the molecules separately and then to group them together to form the crystal structure.

It is important to realize that the framework on to which we fit the ions, atoms and molecules consists only of " construction lines," which have no correspondence to the bonds which hold the crystal together. The bonds, irrespective of their type, exist between neighbouring atoms and the resulting arrangement is regular simply because this gives lower energy. The use of the " construction lines " is that we can describe the crystal structures most easily by reference to them, and also that they render the technique of X-ray crystal structure determination easier.

CHAPTER VI

Common Salt and Diamond

> "We doubted whether the detailed images, by which we try to visualize the structure of matter, might be thought of as 'really existing' in the same sense as palpable objects around us, this fruit basket for instance. Do they resemble the latter in being the scaffolding for a series of *perceptions*, which can be conceived, if not actually experienced? We were allowed to answer this question in the affirmative in many cases, such as the space-lattice of atoms in a crystal."
> —ERWIN SCHRÖDINGER, *Science and the Human Temperament*.

In a previous chapter we have seen that crystals can be divided into four main groups, ionic, homopolar, metallic and molecular, according to the type of binding which exists between the atoms. The crystals belonging to any one group have many features in common, so that a detailed consideration of one typical member gives a general idea of the nature of the group as a whole. The groups are not, however, rigid categories, for there are a large number of crystals which represent a transition from one group to another. In purely ionic crystals an electron is actually transferred from one atom to another, resulting in an electrical attraction between the ions so formed; in purely homopolar crystals two electrons are shared equally by neighbouring atoms. It is evident that if we have electrons which are transferred for part of the time but are shared for the remainder, we shall have a type of binding intermediate between ionic and homopolar. These bonds will have properties intermediate in nature between ionic and homopolar bonds. They will tend to be in fixed directions, as in homopolar crystals, but the number of neighbours around any one atom will be too great to allow two electrons to each bond. We shall return later to these " transition " types of crystal in a few cases of special interest and importance.

The crystals which we have chosen as typifying their groups are:

Common Salt (sodium chloride).—This is one of the best-known ionic crystals.

Diamond.—In diamond, which is one form of the element carbon, we have a perfect example of a homopolar crystal.

Copper.—This metal has one of the three typical metallic structures. It was also the first metal to be used for X-ray diffraction experiments.

Paraffin Wax.—This substance has been chosen since its properties are very familiar. We shall see how it is built from packing molecules together.

The contrasts between the groups are evident from a consideration of the more obvious physical properties of these crystals. A few of these are listed on page 49.

COMMON SALT (SODIUM CHLORIDE)

Soon after Laué's discovery of the diffraction of X-rays by crystals, W. L. Bragg, who has played a vitally important part in the development of X-ray crystallography, was investigating at Cambridge the diffraction patterns obtained with thin sheets of mica. Mica has a very complicated structure, and, though its structure is now known, it would have been impossible to discover it with the methods then available. Sir William Pope, who was associated with Barlow (p. 24) in suggesting the possible structures of crystals, prior to the discovery of the X-ray method, had realized that sodium chloride and potassium chloride should have fairly simple

PHYSICAL PROPERTIES OF CRYSTALS

	Common Salt	Diamond	Copper	Paraffin Wax
Melting-point.	804° C.	Changes to graphite at over 2000° C.	1083° C.	About 50° C.
Electrical conductivity.	Very small, probably due to impurities and imperfections.	None.	Very large.	None.
Transparency.	Transparent.	Transparent.	Opaque.	Transparent.
Refractive index.*	1·54.	2·42.	Can only be found indirectly.	About 1·46.
Mechanical properties.	Hard.	Hard.	Fairly soft.	Soft.
	Plastic when stretched, but brittle under a blow.	Brittle.	Plastic.	Plastic.
	Cleaves.	Cleaves.	Glides.	Probably cleaves.

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* See footnote on p. 76.

structures. So he suggested the study of these compounds to W. L. Bragg, with the result that the first crystal structure was determined. E. Madelung had also predicted the structure from certain physical properties. This structure is illustrated in fig. 25 and Plate IV*a*, but before describing the structure and the construction of a model, we will give some consideration to the reasons why sodium chloride has the structure which W. L. Bragg found.

The neutral sodium atom has eleven units of positive charge on the nucleus and eleven electrons circulating round it. These are in groups 2, 8, 1, and the outer electron is easily removed, leaving a singly charged positive ion. The chlorine atom has seventeen units of charge on the nucleus, and the electrons are arranged in the groups 2, 8, 7. The singly charged negative ion is easily made by adding an electron to the outer group.

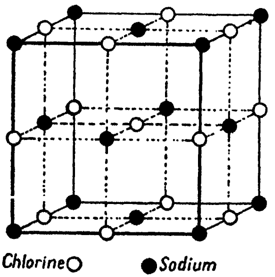

Fig. 25.—Common Salt (Sodium Chloride)

In the sodium chloride crystal all the sodium atoms have lost their electrons to chlorine atoms, so that the units from which the structure is built are sodium ions with a single positive charge, and chlorine ions with a single negative charge. The radii[*] of the ions are: sodium, 0·98 Å. and chlorine, 1·81 Å. It is interesting to note that when the sodium atom loses an electron to make the ion, the radius decreases from 1·86 Å. in metallic sodium to 0·98 Å.

Each sodium ion tries to collect around itself as many chlorine ions as possible, owing to the electrical attraction between its positive charge and the negative charge on these ions. There are two agencies at work to prevent the number of chlorine ions surrounding any one sodium ion becoming very large. The first is that not more than a certain number can be packed round one sodium ion, owing to their relative sizes; the second is that each chlorine ion is endeavouring to surround itself with sodium ions. The radius of the chlorine ion is so much larger than that of the sodium ion, that only six chlorine ions can be packed round one sodium ion. This number six is called the " co-ordination number " of the sodium ion for chlorine.

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[*] These radii are actually found from crystal structure measurements of the distance between ions. The main difficulty in obtaining them is that we usually only know the sum of the radii of positive and negative ions from the X-ray results. However, by using certain exceptional cases where one radius can be found, the rest can be obtained by subtraction.

In order to give an ionic crystal the maximum stability, the positive and negative ions must be as close together as possible. The electric charges will, therefore, effectively be neutralized between neighbouring ions. We have seen that each sodium ion has six chlorine neighbours, which, since there are no directed bonds, are regularly arranged around the central ion. Since the charge on the sodium ion is one positive unit, we can measure the strength of the bond between it and one of its chlorine neighbours as being one-sixth.* Therefore each chlorine ion must receive one-sixth of its total bond strength from a sodium ion, so that each chlorine ion must have six sodium ions around it. Since sodium is so much smaller than chlorine, many more than six sodium ions could be packed round one chlorine ion, if the only limitation were geometrical. But the limitation to six follows as a necessary consequence of the electrical forces between ions, which require the whole crystal to be neutral and also that the neutralizing should mainly be achieved by nearest neighbours neutralizing their charges.

Sodium chloride is, then, made up of sodium and chlorine ions, each of which is surrounded by six ions of the other. This condition has not determined the structure, since there are several ways of building structures with these co-ordination numbers. The further point we require to fix the structure is that, for a purely ionic crystal, a regular arrangement is more stable than an irregular arrangement. So the sodium and chlorine ions arrange themselves in the highly symmetrical way shown in fig. 25 and Plate IV*a*.

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* For an ion of charge m with n neighbours, we have a bond strength m/n which equals $\frac{1}{6}$ for chlorine and sodium in sodium chloride.

Experiment 9.—Construction of a model of sodium chloride. The cubic framework (p. 44) is used. One coloured plasticine is used for sodium and another for chlorine; if plastone is being used to make a permanent model, the balls can be painted. Then the sodium ions are on a face-centred cubic arrangement, so the plasticine for each sodium ion is attached at the positions *A* and *B*, i.e. at the corners of the cube and the centres of the faces. The plasticine corresponding to chlorine is fastened at positions *C* and *D*. The rest of the crystal can be pictured as being built by repeating this unit cell indefinitely. On examining the chlorine atom at the body centre *C*, it can be seen at once that its nearest neighbours are the six sodium ions at the centres of the faces. By building or sketching a little more of the structure it is easy to see that each sodium has six chlorine neighbours. The face-centred lattice of sodium ions is exactly similar to the lattice of the chlorine ions, but the two have been moved half the side of the cube relative to each other.

The high symmetry of the sodium chloride arrangement is evident, and, as we know, crystals of common salt are almost always found in nature in the form of cubes. The forces binding the ions together are strong and the structure is fairly compact. So the crystals are hard and not very easily distorted when dry. We can see also that it would be difficult for an ion to move through the structure, and this is the reason why sodium chloride is not a good conductor, though in solution, when the ions are free of each other, they serve as carriers of electricity.

DIAMOND

Diamond was another of the early structures to be discovered. The outstanding characteristics of diamond crystals naturally attracted the interest of the early X-ray workers, so the structure was determined as early as 1913, by Sir William Bragg and W. L. Bragg, working in collaboration. In the early days only the simpler crystals could be investigated satisfactorily, which was the reason why the substances studied were mostly of cubic symmetry. The structure is illustrated in fig. 26, and as in the case of sodium chloride, we shall now consider why carbon atoms should arrange themselves as we actually find them, before describing how to make a model of the structure.

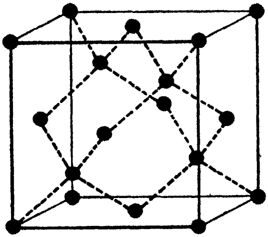


Fig. 26.—Diamond

We have already seen that carbon atoms have six electrons, arranged in groups 2, 4, and each atom usually combines with other atoms by forming homopolar (electron pair) bonds with them. Carbon can form four of these homopolar bonds, since it has four electrons in its outer group and so requires four more to make the number up to eight. In diamond, carbon combines with itself—the electron pair bonds are between neighbouring carbon atoms—so that the basis of the diamond structure is that each carbon atom is surrounded by four other carbon atoms linked to it by these homopolar bonds. The atoms are held together by a mesh-like network of bonds in space, and the actual way this is achieved is shown in fig. 26. The drawing only shows the unit of the pattern, but if we imagine this unit repeated indefinitely we can see how the bonds form an unlimited network.

Experiment 10.—Construction of a model of diamond. The carbon atoms occupy positions *A* and *B* on our cubic framework, and also the four positions *E*, one-quarter and three-quarters of the way down a diagonal. Plasticine, or plastone for a permanent model, is placed at these points. The four positions *E* are shown in fig. 24, but we shall give a further description of how to locate them. If we are looking down on the framework, then two of the carbon atoms in position *E* are one-quarter of the way down the diagonals, on opposite sides of the face-centring point. Then, still looking down on the cube, the atoms three-quarters of the way down the diagonals will appear to be in the small squares left unfilled by the atoms one-quarter of the way down. Thus, if we divide the cube into eight little cubelets by halving all the sides, no two carbon atoms in position *E* are at the centres of neighbouring cubelets. Having placed the carbon atoms, it is necessary to illustrate the bonds between the atoms. Each of the atoms in the cubelets has four neighbours, and if plasticine or plastone has been used for the atoms, short lengths of wire can be inserted between the atoms to represent the bonds. It will then be seen that each carbon atom has four bonds distributed evenly in space. The side of the unit cube of diamond is 3·56 Å. and the distance between neighbouring carbon atoms is 1·54 Å.

It is the even distribution of bonds in space, together with the strength of the pure homopolar bond, that gives diamond its great hardness and perfect crystalline structure. The flaws in diamond are rarer than in any other crystal, and so it is regarded as typical of a perfectly regular internal structure. In sodium chloride, there may be very fine cracks or slight irregularities, since the bonds have no directional character which would enable them to resist distortion, but in diamond all kinds of distortion are prevented. Thus diamond is unique not only in the world for its value, but also in the world of crystallography for its perfection of structure.

CHAPTER VII

Copper and Paraffin Wax

> " Now the smallest Particles of Matter may cohere by the strongest Attractions, and compose bigger Particles of weaker Virtue; and many of these may cohere and compose bigger Particles on which the Operations in Chymistry, and the Colours of natural Bodies depend, and which by cohering compose Bodies of a sensible Magnitude."
>
> —SIR ISAAC NEWTON, *Opticks.*

The specimens of the metal copper with which we are familiar are not single crystals. They are made up from a vast number of grains, each of which is a single crystal, though these crystals have no regular external faces. Each little grain in a piece of copper has a regular internal structure. This multitude of small single crystals is an extreme case of the result of allowing a substance to crystallize so that the growth of one crystal interferes with that of another.

The properties of copper depend on two factors, the properties of each grain separately, and the way the grains are packed together. The processes of drawing wire, or making foil, change the packing of the grains, and give the wire and foil properties appreciably different from those of the metal in bulk. For the moment we are only concerned with the nature of an individual grain and the regular arrangement of the atoms of which it is composed. It is possible to obtain single crystals of copper, and it is in this form that copper is found native in minerals. Single crystals of copper with plane faces are found in the Lake Superior Mining

Region, often enclosed inside crystals of calcite. The crystals have, occasionally, cube and octahedron faces developed, which reveal the cubic nature of the metal.

The copper atom has twenty-nine electrons arranged in groups 2, 8, 18, 1. In the metal the single outer electron is more or less free, serving to bind the positive ions together. Thus, since these ions are spherical, the structure will be essentially one of spheres packed as closely together as possible. The space occupied by the free electrons is accounted for by treating the atomic radius used in metals as including the electrons.

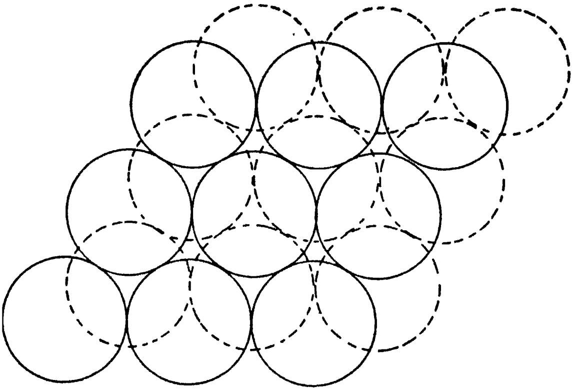
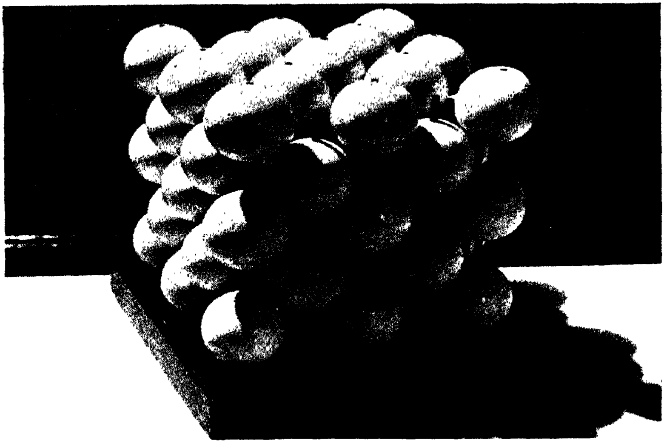
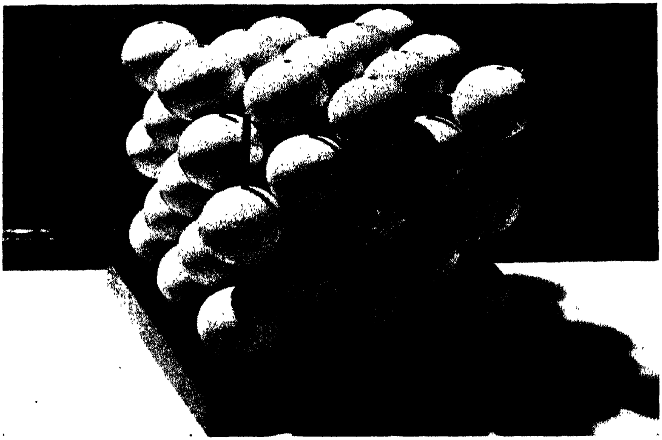


Fig. 27.—Hexagonal Close-Packing

To elucidate the structure we must, then, imagine what happens when we pack spherical balls together. If we take a number of balls on a table and push them together, then each ball will be surrounded by six neighbours. This is shown by a layer of the arrangement in fig. 27, which is a representation of how the balls would look from above the table. Now, if we take several layers of this type and pile them on one another, we shall obtain the types of close-packed structures.



(*a*) Cubic Close Packing



(*b*) Cubic Close Packing—one layer removed

Figs. 27 and 28 show the two most common ways in which the layers are fitted together. Each ball in one layer rests between three in the layer above and three in the layer below. In the first case (fig. 27), the layer above and the layer below have corresponding balls directly over each other. In fig. 28, on the other hand, the balls of the layer above lie between three balls between which there is no ball on the layer below. A fourth layer has to be added to repeat the positions of the bottom layer. In either case any one ball has twelve others in contact with it. The marked hexagonal appearance of the first arrangement is easily seen, and so this structure is called " hexagonal close-packing ". It is illustrated in fig. 51 and in Plate III*b*, and is a common structure among metals, though it is not possible to induce copper to crystallize in this way.

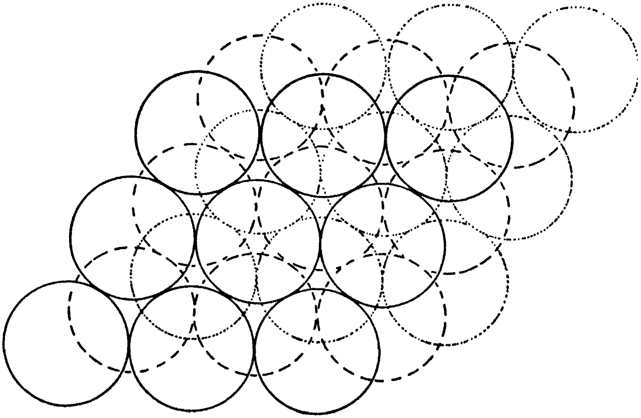


Fig. 28.—Cubic Close-Packing

The second method of arrangement is that corresponding to copper. The direction along which we have been packing the layers is actually one of four threefold symmetry axes in this structure, and the presence of these axes makes the structure cubic in symmetry. In Plates II*a*, *b* and III*a*, this is emphasized. The copper atoms are arranged at the corners of the cubes and at the face-centring positions. Actually Plate II*a* shows a block of eight of the unit cubes, each side of the block being twice that of the unit cube. The three diagrams show successive layers removed along the diagonal, which is one of the four threefold axes. The familiar appearance in Plate III*a* of each atom with six surrounding it shows us that the diagram does represent a close-packed structure. The atom at the corner in Plate II*a* lies between the three atoms beneath it shown in Plate II*b*. Then if we examine Plate III*a* carefully, we can see that no atom lies between these three in the third layer, this position being a gap between three atoms. This exactly corresponds to our second method of close-packing, which is illustrated in fig. 28. We may call the structure " cubic close-packing ". It is also called the " face-centred cubic " structure, but the first name is to be preferred since it emphasizes its relationship to the hexagonal close-packing. Many metals crystallize in this arrangement.

Experiment 11.—Construction of a model of copper. (a)

Take a number of celluloid (ping-pong) or wood balls of equal size. Glue six to one of them, so that all seven are in one plane (as in fig. 27), and make four layers of this type. Then by fitting these one on the other, build the hexagonal and cubic close-packings. Only three layers are necessary for hexagonal close-packing and four for cubic, since additional layers merely repeat the pattern. This cubic close-packing is the structure of copper.

Experiment 12.—Construction of a model of copper. (b)

Make a unit cell of cubic close-packing, which is the structure of copper, by placing plasticine on the cubic framework at positions *A* and *B*. Turn the cube so that a diagonal is vertical and compare the structure with the cubic close-packing of Experiment 11. It will be seen that, if the unit cell were repeated indefinitely, the atom centres on the framework would coincide with the centres of the balls. Thus the two structures are exactly the same.

It is evident that the layers of close-packed atoms can easily slide over each other, and it is to this "gliding" of the layers that copper owes its ductility and malleability. When a copper wire is pulled out, each little crystal grain is deformed, and the planes of atoms slip over each other. This slipping also alters the arrangement of the small crystals and so modifies the properties of the wire. All these changes can be followed by means of X-rays, using the methods discovered in 1916 by Debye and Scherrer, and also in 1917 by Hull.

In copper there are four sets of planes, perpendicular to the four threefold axes, in which gliding can take place. So when a single crystal of copper is pulled out, the changes are rather complex. In a hexagonal close-packed crystal, there is only one set of close-packed planes, at right angles to the sixfold axis, which can glide over each other. Figs. 29 and 30 show the changes which result from this gliding. Fig. 29 is a section of a rod of single crystal before gliding occurs, while in fig. 30 the rod has been pulled out, causing the planes to slip over each other as if the crystal were a pack of cards. Each figure is actually the section of the rod which includes the direction in which the gliding is occurring. Gliding does not affect the thickness at right angles to this direction, so the rod is pulled out into a thin ribbon. Single crystals of cadmium (cadmium has a structure which is very nearly hexagonal close-packing),

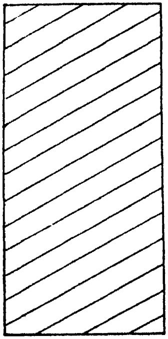


Fig. 29

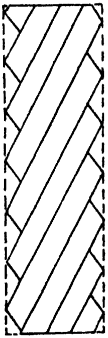


Fig. 30

which are in the shape of rods, can be pulled out by hand to three or four times their original length before breaking, whereas it is impossible to stretch an ordinary cadmium wire of the same size without quite large forces. This shows how, in an ordinary metal made from innumerable small crystal grains, the grains mutually assist each other in resisting any deformation.

PARAFFIN WAX

Paraffin wax is made up of a mixture of compounds of hydrogen and carbon, in which the carbon atoms are linked together in chains. One compound differs from another only in the number of carbon atoms which are linked together to form the molecule. The compounds are members of the paraffin series of hydrocarbons. As in the case of the metal copper, the wax which we are accustomed to handle is made up of a large number of more or less perfect single crystals, jumbled together. Single crystals of the various members of the paraffin hydrocarbons can be prepared, and it is with these that Müller has done some of the more important work in determining the X-ray structure of these compounds.

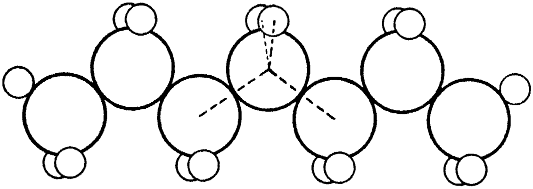
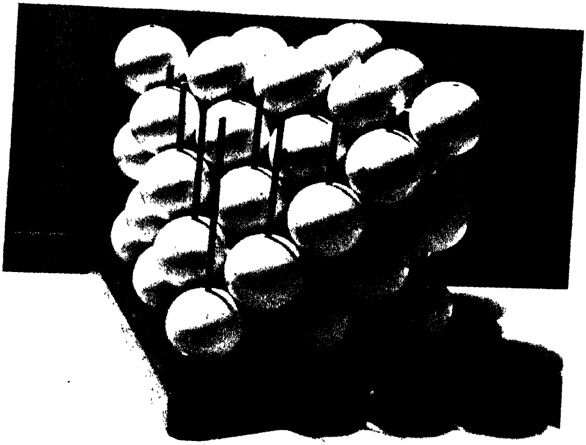
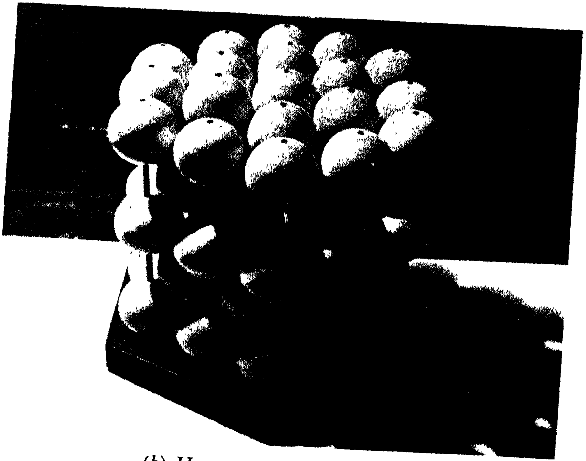


Fig. 31.—Molecule of Paraffin Hydrocarbon with Seven Carbon Atoms

In the three crystals we have discussed so far the bricks from which the structures are built are the ions and atoms, but for molecular compounds of which paraffin wax is typical,



(*a*) Cubic Close Packing—two layers removed



(*b*) Hexagonal Close Packing

we can first consider the structure of the molecule and then consider how these molecules are packed together under the action of the weak residual forces.

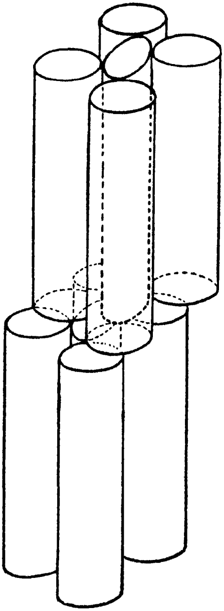


Fig. 32—Packing of Paraffin Molecules in the Crystal

A molecule of one of these paraffins is made by linking carbon atoms together to form a zigzag chain. Each carbon atom forms, as we have already seen, four bonds arranged tetrahedrally. So the end atoms of the chain can combine with three, and the atoms in the chain with two, more atoms. In the hydrocarbon these bonds are made with hydrogen, so each atom in the chain is linked with two hydrogen atoms, and the end atoms are linked with three. X-rays cannot locate these hydrogen atoms, since they do not scatter the X-rays appreciably, but the zigzag nature of the chain (fig. 31) has been verified.

If we take a number of solids of roughly the same shape as the chain molecule, and pack them together, we obtain the structure of a pure paraffin hydrocarbon, as in fig. 32. The ordinary wax is made from a mixture of molecules which differ in length, the proportions of the various lengths depending on the source of the wax. These differences do not affect the structure very much as they are small compared with the chain length.

The weakness of the binding between the molecules in paraffin wax explains not only its softness but also its low melting-point. With the increase in motion of the molecules when the temperature is raised, the forces between the molecules are no longer powerful enough to restrain the motion within limits, and so the solid melts.

When the wax is warmed, the chains commence to rotate about their axes before the whole arrangement becomes random and melting occurs. Thus, instead of having to pack bodies for which the breadth is greater than the width, we now have to pack together cylindrical rods. These naturally arrange themselves so that each cylinder is in contact with six others, so that the structure is built up of layers of rods packed closely together. Each layer fits into the layer above and below so that the end of every cylinder is packed snugly between the ends of three cylinders in the next layer. So, except for the distortion which results from using cylinders instead of spheres, we have a hexagonal close-packed structure. The transition from one form to the other is very easily effected, since the structure before rotation sets in is very similar to this.

SUMMARY

We may perhaps summarize, briefly, the four structures which we have taken as representing the four main crystal types.

In sodium chloride, each ion is surrounded by six ions of the opposite charge, making the whole structure electrically neutral. The crystal is bound together by the powerful forces of electrical attraction, together with weak residual forces. In diamond, each carbon atom is bound by homopolar (electron pair) bonds to four neighbours, thus building up an interlocked three-dimensional network. This contrasts markedly with copper, in which the ions are bound together as closely as possible by the free electrons. The structure can be obtained from the close-packing of spheres. Paraffin wax is built in two stages, the first of which produces the molecule of a long chain hydrocarbon, and the second packs these together to form the crystal. Copper and wax, as normally obtained, are made by packing these single crystals together.

In succeeding chapters we shall consider, in much less detail, other typical representatives of crystals in the four classes, ionic, homopolar, metallic and molecular. We shall also try to illustrate the general laws of architecture in each class.

CHAPTER VIII

Ionic Crystals

> " The wide class of ionic crystals, including the metallic oxides and salts and all the petrogenic minerals, has been more studied, and more successfully, than any other branch of crystal chemistry. From a theoretical standpoint this is because the ions of which they are composed are of definite charge and radius, so that compounds formed from them can only depend on these two variables, and on the relative numbers of ions of each kind that are present."
>
> —J. D. BERNAL.

In Chapter VI we considered the structure of a typical ionic compound—common salt. In the present chapter we shall consider some of the more important ionic structures, with a view to discovering the principles underlying their construction. In so wide a field it is essential to introduce some method of classification which divides the host of ionic compounds in a manner corresponding to their structural differences. From this classification, the rules of architecture of ionic crystals will be seen more clearly than by a mere description of a large number of structures.

The first method of classification of ionic crystals is by the ratio of the number of positive ions to the number of negative ions. For crystals made from two types of ion only, this ratio gives the same classification as the ratio of the charges on the ions. This follows since the crystal as a whole is electrically neutral, giving (the charge) × (number of positive ions) = (the charge) × (number of negative ions).

In sodium chloride we have one chlorine ion for each sodium ion, so the ratio is 1 : 1. Compounds of this type we may call AX compounds, where A stands for the positive and X for the negative ion. In calcium fluoride we have seen that there are two fluorine ions for each calcium ion, so we can represent this type of compound as AX_2, the 2 indicating twice as many X ions as A ions. We can also obtain AX_3 compounds (e.g. aluminium chloride), and A_2X_3 compounds (e.g. one of the iron oxides). It is easy to appreciate that structures of AX_2 compounds are very different from AX compounds, since we have to fit in twice as many negative ions.

The second factor which influences the structure of ionic crystals, and, as a consequence, must be incorporated in our consideration of classification, is the "purity" of the ionic attraction. A purely ionic attraction has no directional character, but partial ionic bonds are known in which there is a tendency to form directional electron-sharing bonds. This directional character profoundly modifies the crystal structure—usually rendering it more complicated by distorting one of the simpler structures. The action of one ion on another in causing a deviation from the pure ionic attraction is called "polarization", since it is the result of the disturbing influence of one ion on the electrons of its neighbours.

AX COMPOUNDS

In these compounds we have the same number of positive ions as negative, so (as we saw for sodium chloride) the number of negative ions surrounding any positive ion is equal to the number of positive ions surrounding a negative ion. We will suppose that the negative ion is larger than the positive ion. This is nearly always true, but if it is not true the following argument can still be applied, if we reverse the rôles of the positive and negative ions.

The number of negative ions which we can pack round one positive ion will depend on their relative sizes. If the negative ion is only slightly larger than the positive ion, we shall be able to pack a large number of them round the ion, giving a high " co-ordination number ". If, on the other hand, the negative ion is very much larger than the positive, only a few ions can be packed around the positive ion, and the co-ordination number will be small. If we take the ratio (radius of the positive ion)/(radius of the negative ion) as the measure of the relative sizes, we find the following co-ordinations:

RELATION OF CO-ORDINATION NUMBER TO RADIUS RATIO

$\frac{\text{Radius of Positive Ion}}{\text{Radius of Negative Ion}}$	Co-ordination Number (Number of negative ions round one positive ion)
Greater than 0·732	8
0·414 to 0·732	6
0·225 to 0·414	4
0·155 to 0·225	3

It is seen that we omit the co-ordination numbers 5 and 7. This is because regular arrangements cannot be obtained using these co-ordination numbers, and an irregular arrangement would be much less stable than a regular arrangement with a lower co-ordination number.

If balls of various sizes can be obtained, these co-ordination numbers can be tested experimentally. Suppose that we have four balls of radius 1 cm., and one ball of radius between 0·225 cm. and 0·414 cm. Then we can arrange the four balls round the smaller ball so that they are all in contact with it but do not touch each other. Since the four balls actually represent negative ions, they must be imagined as repelling each other, and so they will arrange themselves at the corners of a tetrahedron surrounding the central ball. If, however, the radius of the smaller ball is less than 0·225 cm., then the four balls can be stuck together, leaving a space inside, in which the smaller ball can rattle about. This arrangement, in which the balls representing the negative ions are in contact, is not found in crystals, but instead three ions are found surrounding the smaller ion. Similar experimental tests can be used to confirm the other co-ordinations.

The geometrical method of finding the co-ordination number is not rigid, since it is evident that " polarization ", the tendency to form directed bonds, will change the co-ordination. This effect is most marked when the positive ion is small and highly charged, since then it exerts a powerful attraction on the electrons of the negative ions. Corresponding to each co-ordination number we find one or more types of structure. We shall describe some of the simpler of these types.

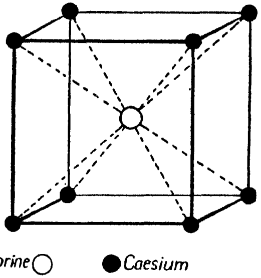


Fig. 33—Caesium Chloride

Co-ordination Number 8.—The typical representative of an ionic structure with eightfold co-ordination is cæsium chloride. Cæsium is a metallic element closely related to sodium and potassium (its electronic structure is 2, 8, 18, 18, 8, 1) and its ionic radius is 1·65 Å. The chlorine ion has a radius 1·81 Å., so the ratio of the radii is 0·91, which corresponds to a co-ordination number 8. If we place the cæsium ion at the corners of a simple cubic lattice, and the chlorine ion at the centres of the cubes, this gives the correct co-ordinations, for each ion has eight neighbours. The structure is illustrated in fig. 33 and Plate IV*b*.

Experiment 13.—Place plasticine representing cæsium at the positions *A* on the cubic framework, and plasticine representing chlorine at position *C*. It is evident that each chlorine ion in the structure obtained by repeating this unit will have eight cæsium neighbours. Show that each cæsium ion will have eight chlorine neighbours.

Co-ordination Number 6.—The most important example of this type is the sodium chloride structure. The radii are, for the sodium ion, 0·98 Å., and for the chlorine ion 1·81 Å., so the ratio is 0·54, corresponding to a co-ordination number 6. This we have already seen is that actually present in the structure. Among the substances which have this structure we may mention silver chloride, quick lime (calcium oxide), magnesia (magnesium oxide), sylvite (potassium chloride), and all the other compounds of fluorine, chlorine, bromine and iodine with lithium, sodium and potassium.

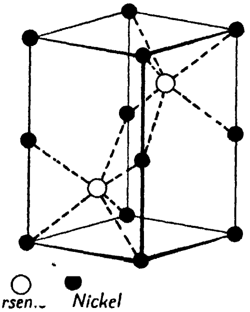


Fig. 34.—Nickel Arsenide

Another important type is the nickel arsenide structure, but this represents a different type of binding, which is partly homopolar and also has some metallic properties, since free electrons are present. This structure is illustrated in fig. 34.

Co-ordination Number 4.—In diamond the co-ordination number was four, so that if we place our positive ions in half the positions of the diamond structure and the negative ions in the other half, we shall obtain a four co-ordination structure. Zinc blende (zinc sulphide) is an example of this type of structure. The radii are: zinc, 0·83 Å., sulphur, 1·74 Å., so the ratio is 0·477. Thus the structure should, according to our rule, be six co-ordinated, but the discrepancy is due to polarization effects of the small highly charged zinc ion. This structure may, indeed, be regarded as homopolar, but it is convenient to include it at this point since it fits into our geometrical scheme. The structure is illustrated in fig. 35.

Experiment 14.—Place plasticine for the zinc ion at positions *A* and *B* on the cubic framework, and for the sulphur ion at the four positions *E* described for diamond. The co-ordinations can then be seen clearly.

Zinc sulphide crystallizes in two forms, zinc blende and wurtzite. The structure of wurtzite is related to that of zinc blende in very much the same way as hexagonal close-packing is to cubic close-packing. If we consider the arrangements of the ions separately, then the relation is exact, for each ion is arranged as in close-packing. Zinc blende is built from zinc ions in a cubic close-packed arrangement and from sulphur ions arranged in another close-packed arrangement, but moved relative to the first so that each sulphur ion falls between four zinc ions. Wurtzite is similarly constructed, but it is based on hexagonal close-packing. The unit cell of wurtzite is shown in fig. 36.

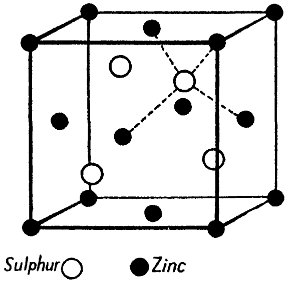


Fig. 35—Zinc Blende

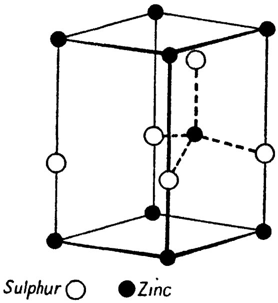


Fig. 36—Wurtzite

It must be emphasized that these considerations of geometrical limitations on the structure, owing to the relative sizes of the ions, furnish only a rough guide to the probable structure. The more comprehensive method is to evaluate the energy of all probable structures for any given compound, and to see which is the lowest. Then this structure will be the most stable, and will correspond to the actual crystal. In making this calculation allowance has to be made for the attractions and repulsions between the ions, their polarizing effect on each other, and also the residual forces which we have seen act between every atom or ion (p. 39). By calculations of this kind M. Born and his collaborators have satisfactorily accounted for the structures of the compounds of sodium, potassium, rubidium, and cæsium with fluorine, chlorine, bromine and iodine. These compounds all crystallize in one of the two types, sodium chloride and cæsium chloride, which we have already described. It can be seen, however, that calculations of this type are extremely laborious to carry through, and so our rough rules, if applied with discretion, are very useful.

AX_2 COMPOUNDS

We will now consider the type of compound in which there are twice as many negative ions as positive, which must necessarily mean that the charge on the positive ion is twice that on the negative ion. In order to examine the co-ordinations in this type of compound we will take a typical case. We will suppose that the positive ion has eight negative ions as neighbours, and that the charge on the positive ion is two units. The problem is to find how many positive ions surround each negative ion. The strength of the ionic link between positive and negative ion is equal to the charge on the positive ion, divided by the number of negative ions surrounding it, i.e. $2/8 = 1/4$. Since the charge on the negative ion is one unit, we see that, in order that the ionic charges may be neutralized locally, each negative ion must have four positive ions as neighbours. So in this case we may write the co-ordinations of the two ions as 8 : 4. In general, for this class of compounds, the positive ion will have twice as many neighbours as the negative ion. If it is the negative ion which has the double charge, then the co-ordination is 4 : 8, or 3 : 6, &c.

The same geometrical limitations on the structure occur for these compounds as for the AX compounds, so we find the types of structure divided up according to whether the co-ordinations are 8 : 4, 6 : 3, or 4 : 2.

Co-ordination 8 : 4.—The most important structure with this co-ordination is fluorspar (calcium fluoride). The calcium ion is, as we have seen (p. 34) doubly charged and the fluorine ion is singly charged. The radii are, calcium ion 1·06 Å. and fluorine 1·33 Å., so the ratio is 0·8, corresponding to an eightfold co-ordination of fluorine round the calcium ion. The calcium ions lie on a face-centred cubic lattice and the fluorine ions occupy the centres of the eight cubelets. This arrangement can be seen in fig. 37.

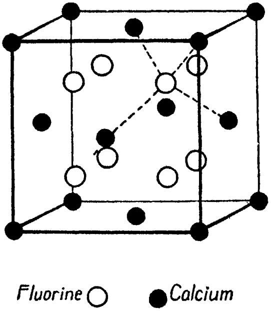


Fig. 37—Fluorite (Calcium Fluoride)

Experiment 15.—Place plasticine representing the calcium ions at positions A and B on the cubic framework. Place also plasticine representing the fluorine ion in all the positions E and E'. Examine the structure carefully, and by imagining the unit cell repeated, show that each calcium ion has eight fluorine neighbours. It is easy to see that each fluorine ion has four calcium neighbours.

Co-ordination 6 : 3.—The best-known structure with these co-ordinations is that of the mineral rutile, which is one of the forms in which the dioxide of titanium crystallizes. The structure is illustrated in fig. 38 in such a way as to show up the co-ordinations. The lines between the ions in all the diagrams of ionic structures are inserted merely to render the co-ordinations clearer, and they must not be confused with the very real directed bonds which we put in the diamond structure. The unit of the structure in rutile is a rectangular block, two of whose sides are equal; this gives the crystals tetragonal symmetry.

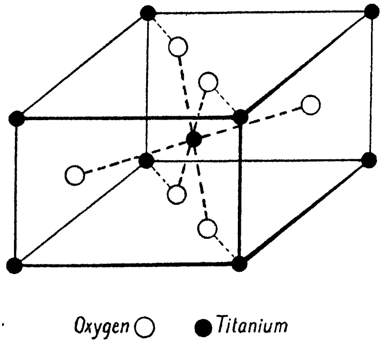


Fig. 38—Rutile
(Titanium Dioxide)

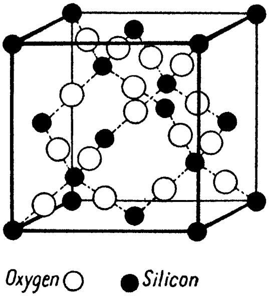


Fig. 39—Cristobalite
(Silicon Dioxide)

Co-ordination 4 : 2.—The most important examples of this type of co-ordination are the various forms of silica, the dioxide of silicon. We shall describe in detail cristobalite, not because it is more important than the forms of quartz or tridymite (all of which are made of silicon dioxide), but because it is a cubic crystal which enables us to build a model of it on the cubic framework.

The structure is illustrated in fig. 39. It is obtained by putting silicon ions in place of carbon in the diamond structure and then inserting the oxygen ions half-way between every neighbouring pair of silicon ions. Thus each oxygen ion is between two silicon ions, and each silicon ion has four oxygen neighbours.

Experiment 16.—Take the diamond structure of Experiment 10 and place plasticine representing oxygen ions halfway along each of the wire bonds which we inserted between the carbon atoms. Then if we take the carbon atoms to be silicon ions, we have a model of the cristobalite structure.

In addition to the regularly arranged forms of silicon dioxide—quartz, cristobalite, &c.—it is possible to obtain a form in which, though the fourfold co-ordination of oxygen round the silicon ion is still retained, the arrangement as a whole is irregular. This form is " fused " silica, or vitreosil, which is a substance similar in appearance to glass. Glass itself is similar in structure to vitreosil, but instead of being pure silicon dioxide, a certain amount of metal oxide (sodium, potassium and lead mainly) has been incorporated into the structure. This change weakens the structure and so ordinary glass melts at a much lower temperature than vitreosil. All substances similar to glass have an irregular arrangement of atoms, which we may call " frozen " in position, so that the atoms cannot rearrange themselves in a regular way.

POLARIZATION AND THE LAYER LATTICES

When the positive ions in an ionic crystal are highly polarizing (i.e. small and highly charged), there is a tendency to form structures made in layers which are only weakly bound together. A layer of the positive ions is enclosed between two layers of negative ions in a kind of sandwich. Then these sandwiches are piled one on top of each other, which results in the negative ion having positive ions as neighbours on one side only; on the other side it is in contact with other negative ions. Fig. 40 illustrates this for cadmium iodide, a compound in which there are two iodine ions for each cadmium, and the co-ordinations are 6 : 3.

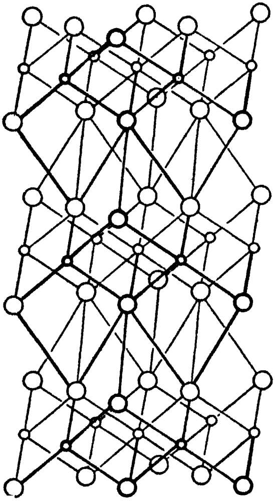


Fig. 40.—Cadmium Iodide

STRUCTURES WITH COMPLEX IONS

We have, so far, only considered ionic compounds in which the units of the structures were ions which were made by changing the number of electrons on single atoms. Ions can, however, be obtained by taking a group of atoms bound together by homopolar (electron pair) bonds and removing one or more electrons from the group.

The most important of these ions are obtained from what are called the " oxyacids ", e.g. nitric, sulphuric, and carbonic acids. The nitrate ion is composed of one nitrogen atom, to which three oxygen atoms are attached by homopolar bonds. In order to form a stable electronic system, the whole group has to gain a single electron, giving it a single negative charge. The three oxygen atoms are evenly spaced in a plane round the nitrogen atom as in fig. 41. The carbonate ion has exactly the same shape as the nitrate ion, being made from a central carbon atom and three oxygen atoms, but in this case the ion has two negative charges.

The sulphate ion is made up of a central sulphur atom, surrounded by four oxygen atoms arranged tetrahedrally, i.e. as evenly as possible in space (fig. 42).

We have mentioned only three of these " complex " ions, but many more are known, some of which contain a dozen or more atoms. Complex positive ions are also known, the most important being " ammonium ", which is made from one nitrogen atom with four hydrogen atoms linked to it, the whole group having a single positive charge.

It is evident that these ions, in general, have a shape which is far from spherical. The shapes of the ions will affect the type of crystal structure of their compounds to a marked degree, so we may make a further classification: (1) ionic crystals with complex ions, (2) ionic crystals without complex ions.

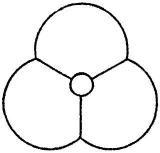


Fig. 41.—The Nitrate or Carbonate Ion

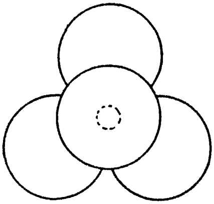


Fig. 42.—The Sulphate Ion

As typical of the structure change produced by introducing complex ions, we may contrast the sodium chloride structure and the structure of calcite (calcium carbonate) and sodium nitrate (Chile saltpetre). Calcite has the same structure as sodium nitrate, for the complex ions have the same shape; the double charges on the calcium and carbonate ions do not affect the type of structure, but only the firmness with which the ions are bound together. The calcite structure is obtained by substituting calcium for sodium in the sodium chloride structure and the carbonate ions for chlorine. Since the complex carbonate ions have threefold symmetry, they are naturally arranged perpendicular to a threefold axis. If we turn the cube so that one diagonal is vertical, then all the carbonate ions are in horizontal planes. This change distorts the cube into a rhomb in the manner shown in fig. 43 and Plate IV*c*. This structure should be compared carefully with that of sodium chloride in fig. 44 and Plate IV*a*. In the plate it is evident that the calcium ions (black) are arranged similarly to the sodium ions (black) in the cubic structure. The carbonate groups can be plainly seen, and also the threefold axis to which they are perpendicular. The unit of fig. 43 is what, on modern ideas, takes the place of our primitive rhomb of Chapter II, and it is from the assembly of such units that calcite is built. In fig. 43 the triangles represent the complex ions, the centres of the oxygen atoms being located at the corners of the triangles.

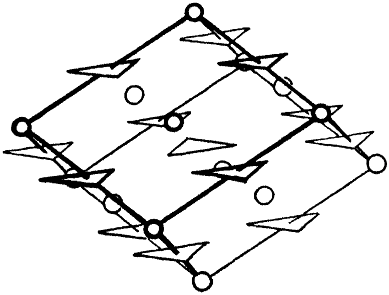


Fig. 43.—Calcite (Calcium Carbonate)

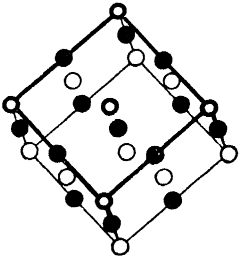


Fig. 44.—Common Salt (Sodium Chloride)

Since all the carbonate complex ions are arranged parallel to one another, the physical properties of the crystal measured in a direction parallel to the plane of the ions will be very different from those measured in a direction at right angles to this plane. The refractive indices * for these two directions were calculated by W. L. Bragg in 1924, and this work illustrates how the properties of matter in bulk can be derived from the atomic arrangement. In the following table we compare the values calculated by W. L. Bragg with those actually observed. The marked difference between the refractive index in the two directions is evident. A qualitative explanation of these results was given by Huygens, who thought the crystal was built from disc-shaped particles.

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* The refractive index is a measure of the extent to which light is bent on passing through a substance. Since calcite has two refractive indices, depending on the vibration direction of the light wave, a beam of light falling on a calcite crystal will, in general, be split into two beams. This is the " double refraction " effect shown so beautifully by the large calcite crystals to which the name Iceland Spar has been given. This effect was studied very fully in the seventeenth century by Huygens.

REFRACTIVE INDICES OF CALCITE

	Calculated	Observed
Light for which the vibrations are in the plane of the carbonate ion.	1·631	1·658
Light for which the vibrations are perpendicular to the plane of the carbonate ion.	1·488	1·486

We have considered calcite as a typical example of this type of structure, and Plate IV illustrates further examples. Calcium carbonate exists in two forms, calcite and aragonite. The aragonite structure is shown in Plate IV*d*, and the carbonate ions can be clearly seen. Plate IV*e* shows the structure of iron pyrites, which was one of the first more complex structures investigated by W. L. Bragg. Iron pyrites is the compound of sulphur and iron in which the proportions of sulphur to iron are two atoms to one. It can be seen from the photograph of the model that the structure is similar to that of sodium chloride, but double sulphur ions replace the chlorine ions. The structure is not, however, that of a pure ionic crystal. The symmetry still remains cubic, but the fourfold axes disappear owing to the unusual way the double sulphur ions are arranged. Plate IV*f* is the structure of anhydrite, calcium sulphate, the components of which are doubly charged calcium ions and doubly charged complex sulphate ions. These complex ions can be clearly seen in the structure.

No new principles are involved in considering these structures with complex ions, except that their shape has to be taken into account when packing together the ions. The forces between the ions are of the same types as those between simple ions.

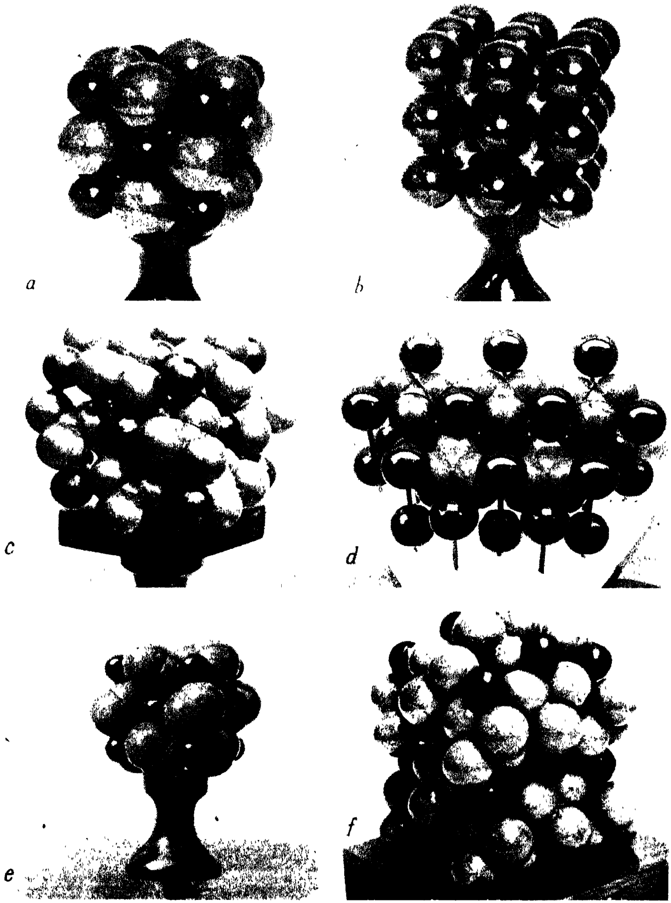
COMPLEX STRUCTURES

We shall not consider in any detail the very complex structures of ionic compounds in which many types of ions are present. Included in this class are the majority of minerals, in particular those of greatest importance from the point of view of mineralogy—the silicate minerals. In 1928 and 1929 L. Pauling formulated the general principles on which these structures are based, and deduced from them the structure of topaz. This forecast was entirely confirmed by an X-ray determination of the structure by Alston and West. The utility and importance of theoretical generalizations is illustrated very clearly by this example. The test of the validity of any generalization is that it should give new results, which can be subjected to a practical test.

We shall endeavour to give the rules in such a form that they connect with the examples of ionic crystals which we have already considered, though, of course, their main usefulness is in handling more complex substances. The whole body of rules is, in reality, an expression of the fact that the arrangement of ions is that of the smallest energy and maximum stability. This means that oppositely charged ions are as close together, and like charged ions as far apart, as possible.

The First Rule.—Every positive ion is surrounded by a number of negative ions, at a distance fixed by the sum of

PLATE IV



a, Sodium chloride. *b*, Caesium chloride. *c*, Calcite, $CaCO_3$.
d, Aragonite, $CaCO_3$. *e*, Iron Pyrites, FeS_2. *f*, Anhydrite, $CaSO_4$.

Crystal Models illustrating the packing together of ions

From "The Crystalline State", by courtesy of
Sir William Bragg and Messrs. G. Bell & Son, Ltd.

the radii of the ions. The number of negative ions around any one positive ion (the co-ordination number) is determined by the ratio of the radii.

The Second Rule.—The charge on any ion is equal to the sum of the electrical bonds from its neighbours. This is the rule which we used to find co-ordinations for sodium chloride (p. 51) and for the AX_2 compounds (p. 70).

The third and fourth rules express the fact that positive ions tend to keep as far away from each other as possible, owing to their mutual repulsion, and the stronger their charge, the greater is this tendency.

The Fifth Rule.—The number of essentially different kinds of constituents in a crystal tends to be small. This means that all like ions tend to have similar neighbours.

These rules effectively connect together whole fields of ionic structures. This is especially true for the silicate minerals, most of whose structures have been obtained by X-ray methods by W. L. Bragg and his co-workers at Manchester University.

We have described ionic structures at some length, because it is in this field in particular that crystallography has made revolutionary contributions to chemistry, in directly determining the arrangement of atoms in space. Its contributions to the chemistry of metals are of great importance, but the results have not reached the same stage of completion that they have in ionic chemistry. Writing to-day it seems strange that chemists were convinced of the existence of a molecule of one atom of sodium and one atom of chlorine in crystals of sodium chloride, but this is really a natural consequence of the historical development of chemistry from the nineteenth-century investigations on gases. It was the absolutely indisputable evidence afforded by X-ray methods, together with the foresight of one or two eminent chemists (Sir William Pope in particular), which led to the general adoption of the present viewpoint.

CHAPTER IX

Homopolar Crystals

"Universals arise merely from our making use of one and the same idea in thinking of all individual objects between which there subsists a certain likeness; and when we comprehend all the objects represented by this idea under one name, this term likewise becomes universal."

—René Descartes, *The Principles of Philosophy*.

In comparison with the other classes of crystal structures, there are very few purely homopolar crystals. We may, however, include in our discussion of these crystals some account of the structures of the elements in which the atoms are bound together in continuous chains, or sheets, by homopolar bonds, the crystals being built by packing these chains or sheets together. The forces holding them together are either solely residual or else partly residual and partly metallic.

In the Periodic Table (Appendix II), neglecting the *A* rows, i.e. the elements in which the inner groups of electrons are being built up, all the elements in column 7 need one electron to complete a rare gas structure. This is achieved by the combination of two atoms sharing two electrons, to form a molecule. It is impossible to obtain any extended purely homopolar structure from these elements. Crystals of them are built from packing together the molecules containing two atoms each.

In column 6 there is a deficiency of two electrons for each atom, which can be made up in several ways, each involving the formation of two bonds. A double bond, in which four electrons are shared, may be formed between a pair of atoms.

This is what is found in gaseous oxygen, the molecule being built from two atoms. A ring of atoms may be formed, each atom in the ring being linked to its two neighbours by single homopolar bonds. The ring molecules are then packed together in the crystals. The rhombic form of sulphur (the form stable at ordinary temperatures) is a beautiful example of this mode of combination. The sulphur atoms are linked together to form a ring of eight atoms, which is not flat but puckered owing to the angle between the homopolar bonds (fig. 45). The third method of linking is to form chains running throughout the structure. As a result of the angle between two homopolar bonds, the chains will not be straight. In crystals of selenium, the atoms are arranged in spiral chains, the whole structure being built from packing these chains parallel to one another. The structure is illustrated in fig. 46. "Plastic" sulphur, which is obtained by pouring the dark viscous molten form of sulphur into cold water, is composed of entangled chains of sulphur atoms. On stretching plastic sulphur, the chains are pulled parallel to each other, a change which can be easily followed by using X-ray diffraction methods. The chains must also exist in the dark liquid and are probably formed by the break up of the eight atom rings at so high a temperature.

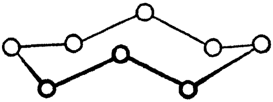


Fig. 45.—The Sulphur Molecule

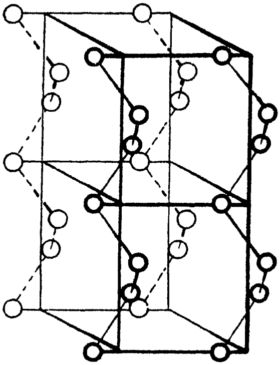


Fig. 46.—Selenium

We may, perhaps, introduce at this point a note on crystals built from chains of atoms. Typical examples of this type of substance are asbestos, wood, cotton, silk, hair and wool. A single fibre of any of these substances is made of a large number of crystals which are very long and narrow. The individual crystals are built from long chains of atoms packed together side by side. Though the atoms are different in these substances (asbestos is made from a double silicon-oxygen chain, whereas cotton and wood are made from a cellulose chain of carbon and oxygen atoms linked together, and wool and hair are built from a nitrogen-oxygen protein chain called keratin), yet there are strong resemblances between the various fibres. These resemblances are the result of the fundamental similarity of structure, each crystal of all of these substances being built from the packing of chains. There are, however, characteristic differences depending on the nature of the chain. The keratin chain can crumple up and then be pulled out again, which gives wool its special properties of being easily stretched and also of shrinking. Chains also exist in rubber, but they are randomly arranged until the rubber is stretched, when, as in plastic sulphur, they are pulled parallel to each other.*

With two bonds at our disposal, it was possible to build a chain, and for elements in the next column (5), which can form three bonds, a sheet of atoms linked together can be built. There are, however, other possibilities. In nitrogen, the three bonds are formed between two nitrogen atoms to form a firmly bound molecule, and no sheet structure is known. Red phosphorus, on the other hand, is built by stacking sheets of atoms together. Any one phosphorus atom in a sheet is linked to three neighbours by homopolar bonds. In the " metallic " forms of arsenic, antimony, and bismuth, a similar type of structure is found. This is illustrated in fig. 47. As we go from arsenic to bismuth, the binding between the layers becomes more metallic, and so the appearance and properties of the elements resemble more and more those of a metal.

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* W. T. Astbury, in *Fundamentals of Fibre Structure* considers all these points in much greater detail.

The elements of the fourth column can form four homopolar bonds and so can build up complete frameworks held together entirely by homopolar bonds. We have already seen how this is achieved in the case of carbon, in the form of diamond. The other elements in this column, silicon, germanium, &c., form structures identical with that of diamond. Carbon, however, can exist in another form, that of graphite.

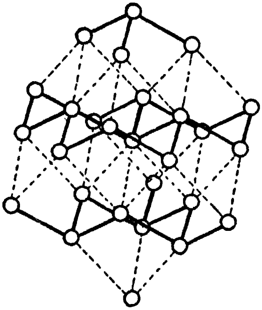

Fig. 47.—Arsenic

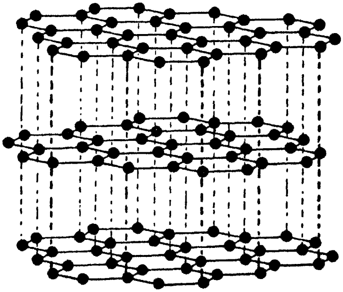

Fig. 48.—Graphite

In graphite, the carbon atoms are arranged in sheets in a pattern similar to that of a honeycomb, so that each carbon atom is linked to three others. The binding of the atoms in these sheets is stronger than if there were only one homopolar bond between each pair of atoms. This extra binding results from the effect of the electrons which form the fourth homopolar bond in diamond. These extra electrons serve as a general binding holding the rings closer together, and so they cannot be attributed to any one pair of atoms in particular. The increased binding draws the carbon atoms closer together, the distance between them is 1·42 Å. in graphite compared with 1·54 Å. in diamond. The layers are packed parallel to each other at a distance of 3·4 Å. (fig. 48), and the binding force between layers is partly residual and partly metallic. This explains the comparatively high conductivity for electricity of carbon in this form.*

Homopolar compounds between elements are formed when the sum of the outside electrons, for one atom of each element, is eight. This number permits the formation of four homopolar bonds, each corresponding to a pair of electrons. One element may contribute more electrons than another, as in aluminium nitride and phosphide, where aluminium contributes three and the nitrogen or phosphorus atom contributes five electrons. All such compounds have either the zinc blende structure (fig. 35) or the wurtzite structure (fig. 36), or some variant of these structures. Carborundum, carbon silicide, is the best example of these variants, since it crystallizes in at least five forms, one of which is the zinc sulphide structure. In all these structures it is extremely probable that each atom will be linked to its neighbours by four homopolar bonds. The strength of the homopolar binding in these compounds is further illustrated by the great hardness of carborundum.

There remains one further class of structures which can be included with the homopolar types—that of the " metallic ores ". This class includes, amongst the structures we have already considered, nickel arsenide and iron pyrites. In these crystals, the metal atoms have incomplete inner electron groups, and the electrons in these groups interact with the non-metallic elements to form bonds which have many resemblances to homopolar bonds. The nature of the ores is not yet fully understood, but it is essential that they should not be regarded as pure ionic crystals.

In this chapter we have seen the difficulties into which any narrow use of classifications would lead us, which emphasizes that any classification is only a convenient method to assist us in tackling our problems.

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* We shall meet these rings again (p. 96), where we shall see that they are fundamental to a large part of organic chemistry.

CHAPTER X

Metallic Crystals

> " I beg of you, therefore, to grant the request of Simplicio, which is also mine; for I am no less curious and desirous than he to learn what is the binding material which holds together the parts of solids so that they can scarcely be separated."—GALILEO GALILEI, *Dialogues concerning Two New Sciences*.

It is very difficult to draw a dividing line between homopolar and metallic crystals. As we saw in the last chapter, bismuth has marked metallic properties, indicating some free electrons. On the other hand the structure is by no means one of a close-packing of spheres. It is, therefore, evident that between diamond, a perfectly homopolar crystal, and copper, a perfectly metallic crystal, we have a continuous range of crystal types.

The most striking characteristics of metals are their opaqueness and their ability to conduct heat and electricity. These properties are all due to the presence of free electrons. A piece of wood, which has no free electrons, can be held at one end while the other end is burning. An iron poker held in the flame will soon become uncomfortably hot, owing to the conduction of heat by the electrons of the metal. The electrons can easily move through the metal and so rapidly transmit the heat motion from one end to the other.

We have considered the principles underlying the structures of ionic and homopolar crystals. For metals we can only consider these principles very briefly as the subject is very wide, including as it does all the structures of alloys; in addition it has not yet been reduced to the same state of order as the study of ionic crystals. The constituents of metals are the free electrons and the atom residues left by the loss of these electrons. The two considerations which underlie all the metallic structures, which do not show any marked homopolar character, are the sizes of the atoms, which include all allowance for the space occupied by the electrons (p. 42) and the action of the free electrons in the electric fields of the ions. In pure metals the size of the atoms is of little importance since all the atoms are identical. In alloys, the difference in size between the atoms of the various kinds of element will mean that certain proportions of the atoms will be able to pack much less wastefully together than others. So we shall get regular arrangements which are the result simply of the relative sizes of the atoms, and which correspond to a close-packing of two or more sets of balls. In these alloys the electrons are serving merely to bind the ions without influencing the structure type.

In contrast to this type of alloy, we have a type in which the identity of the atoms is of little importance, which can only be true if they are roughly of the same size. The controlling factor in determining the structure is the ratio of the number of free electrons to atoms. The development of this conception furnishes another instance of how the scientific method works in practice. In 1925 A. Westgren and G. Phragmén suggested, as a result of their experimental work, that atoms in metals which were in identical positions crystallographically, should be treated as equivalent from the point of view of metal chemistry. This " losing the identity " of the atoms of an element in a metallic alloy was very much counter to the old classical views of chemical union. However, in 1926, W. Hume-Rothery took the further step forward of saying that the resemblance between the structures of certain alloys resulted from the ratio of free electrons to atoms being the same. We will see how this applies for alloys of the same structure in the alloy systems copper-zinc, copper-aluminium, and copper-tin.

ELECTRON-ATOM RATIOS FOR SOME COPPER ALLOYS

Proportions of Atoms of Elements in the Alloy	No. of Atoms	Free Electrons			Ratio Free electrons / No. of atoms
		Copper	2nd Element	Total	
Copper 1, zinc 1	2	1	2	3	3/2
Copper 3, alum. 1	4	3	3	6	3/2
Copper 5, tin 1	6	5	4	9	3/2

Westgren and his collaborators continued their careful investigations, confirming the ideas of Hume-Rothery of the importance of the electron-atom ratio for these alloys. The whole work culminated in the theoretical interpretation of H. Jones in 1934, who showed that the brilliant intuitions of Hume-Rothery are fully confirmed by the application of the quantum theory to these structures.

We may also, of course, get structures in which both the sizes and electron-atom ratios are of importance. Fortunately these alloys are not of such frequent occurrence.

On the basis of these principles we may divide the types of metallic structures into three classes as follows:

1. *True Metals.*—These are metals and alloys in which the size of the atoms is the most important factor. They include: the alkali metals (lithium, sodium and potassium), the alkaline earth metals (beryllium, magnesium, calcium, &c.), the transition metals (from scandium to copper in the table of Appendix II, including the important metals iron, cobalt, nickel, chromium and manganese), and alloys of these elements.

2. *Electron Compounds.*—These are the compounds which Hume-Rothery showed to have structures depending on the ratio of free electrons to atoms, rather than on the nature of the atoms. These alloys are formed from the combination of iron, cobalt, nickel, copper, silver or gold with zinc, gallium, arsenic, cadmium, tin, antimony or bismuth. The sizes of most of the atoms for these elements are very nearly the same (bismuth is larger), so that size need not be considered.

3. *Semi-metals.*—These include zinc, gallium, mercury, tin, and lead. They represent a transition to a homopolar lattice and must be considered as not purely metallic nor yet purely homopolar. With an increasing tendency to form homopolar bonds, the structures depart more and more from close-packing.

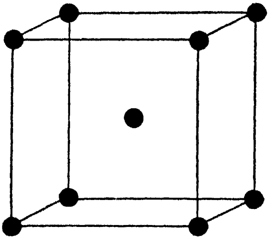


Fig. 49.—Body-centred Cubic Structure

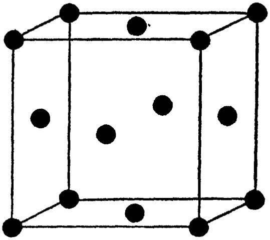


Fig. 50.—Cubic Close-packing

We shall only consider in detail the structures of the true metals. To treat at all adequately the other groups would require much greater space than we have at our disposal.

In Chapter VII we described two of the three structures typical of the elements in this class, cubic close-packing and hexagonal close-packing. In each of these any one atom is surrounded by twelve others. The third common metallic structure is one in which any atom has only eight nearest neighbours, but this is compensated by the existence of six more not a great way farther off. This arrangement is the body-centred cubic structure, illustrated in fig. 49. This may be compared with the close-packed structures in figs. 50 and 51.

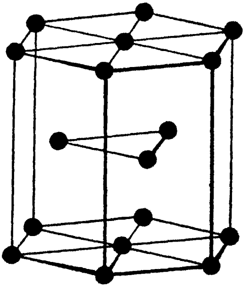


Fig. 51.—Hexagonal Close-Packing

Experiment 17.—Place plasticine in positions *A* and *C* on the cubic framework. Then this represents the unit cell of the body-centred cubic structure.

We have seen that the total energy of certain ionic crystals can be evaluated by adding up the interactions between the ions. In a similar way the total energy of pure metals can be found by adding up the interaction between the ions and the free electrons. It is found that the energy due to the motion of the free electrons is of considerable importance. By their motion, the electrons tend to keep the ions in the metal apart, whilst the attraction between the ions and electrons holds the metal together. This gives us the key to the difference between sodium, which is a soft, very light metal with a body-centred cubic structure, and copper, which is much harder and denser, and has a face-centred cubic structure. In sodium it is almost solely the motion of the free electrons which holds the ions apart. So the metal is easily compressed, and is very soft. Also, since only a portion of the space in the metal is occupied by the ions, the metal is very light. The body-centred structure is the most stable for a metal of this type. In copper, the ions are practically in contact, so the metal cannot be compressed easily, and as almost the whole of the space is occupied by the ions, it is also comparatively dense. Since the ions are held in contact, the structure is close-packed. Numerical calculations of the energy, compressibility, density, &c., have been made successfully for these metals.

The most important difference between the body-centred and close-packed structures is that the absence of close-packed layers of atoms, from which both cubic and hexagonal close-packings are built, makes gliding much less easy in the body-centred structure. So we find that metals with body-centred cubic structures are much less ductile and malleable than the close-packed metals. The structures of the more important metals in these classes are given below:

Cubic Close-packing.—Copper, silver, gold, calcium (below 450° C.), the high temperature form of iron.

Hexagonal Close-packing.—Magnesium, calcium (above 450° C.), one form of cobalt, and one form of nickel.

Body-centred Cubic.—Lithium, sodium, potassium, one form of chromium, iron (at ordinary temperatures).

Iron exists in different forms at different temperatures, which explains its technical importance, since at high temperatures it is malleable, but the structure change on cooling hardens it.

Alloys between elements in this group consist largely of " solid solutions ". A solid solution of one metal in another means that the added atoms replace the atoms of the first metal at random, so that the structure remains unaltered fundamentally. Limitations on the extent of solid solution, for these " true " metals, result from the differences in size of the atoms. As an example we may take the system copper-gold. When the proportions in the alloy are three atoms of copper to one of gold, the gold atoms occupy the positions at the corners of a cube and the copper atoms are at the centres of the faces. Neglecting the differences between the atoms would give us a face-centred cubic or close-packed arrangement. Similarly, when there are three atoms of gold to one of copper, the positions are reversed.

Experiment 18.—Build the structure of the two copper gold alloys. Place one kind of plasticine in positions *A*, and another in positions *B* on the cubic framework. Then this can represent either of the above alloys.

At high temperatures the motion of the atoms, which becomes more violent as the temperature increases, leads to an upsetting of this regular arrangement and the atoms are distributed at random in a cubic close-packed structure. On cooling slowly, the atoms gradually take up the regular positions. The theory of how this process goes on has recently attracted much attention, and the attempts of W. L. Bragg and H. A. Bethe in this field have met, at least, with partial success.

The study of the properties of metals and alloys is of extreme technical importance. It is only now, with a definite method of locating the positions of atoms available, that there is any chance of putting the whole subject of metallurgy on a sound basis. Considering the remarkable achievements of X-ray crystallography in a very short time, the outlook is very hopeful.

It must be remembered that we have only dealt with the constitution of each small grain in a metal. The metal in bulk, as we ordinarily find it, is made from packing together these grains of single crystal. Even this packing yields results on X-ray investigation, in finding the size of the grains and their orientation relative to one another.

CHAPTER XI

Molecular Crystals

" The devil may write chemical textbooks, because every few years the whole thing changes."—BERZELIUS.

In the fields of ionic and metallic chemistry, the discoveries of crystal structure analysis came as revolutionary changes, and in the majority of cases these changes have not yet crept into chemical textbooks. In one field, however, the work of the X-ray crystallographer has confirmed almost in its entirety the work of the chemist. This field is the structure of molecules, which is, to a large extent, concerned with the tremendous variety of carbon compounds which make up the subject of organic chemistry.

A molecule is built by linking atoms together with homopolar bonds. The more or less rigid structure which results from this linking persists as a unit in crystals, so that we have the twofold problem of the arrangement within the molecule and the arrangement of the molecules themselves. We shall, in this chapter, concern ourselves almost solely with molecular carbon compounds.

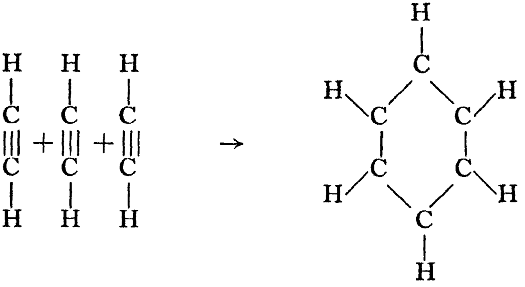
By 1874, the two great principles underlying the structure of carbon compounds had been discovered by chemists. The first of these was that the carbon atom, when combined with four other atoms or groups of atoms, is linked by bonds which are arranged evenly in space. Thus, if we place the carbon atom at the centre of a tetrahedron, the four bonds are directed towards the four corners (fig. 22). This idea was the work of Le Bel and van't Hoff. The second principle, due to Kekulé, was that in benzene, where we have a molecule composed of six carbon and six hydrogen atoms, the six carbon atoms are linked together to form a hexagonal ring. One hydrogen atom is joined to each carbon atom. On the basis of these principles, the structures of both simple and complex organic compounds were discovered, by making use of their various chemical reactions.

The supreme test, from a chemical viewpoint, of one of these structures is to see whether it is possible to make the molecule from simple constituents. Using the structure as the key, reactions are performed between simple substances, gradually linking them together in suitable positions, until finally the whole structure is built up. A simple instance of this is given on p. 94, the symbols being: C, carbon; H, hydrogen. Each line represents a bond.

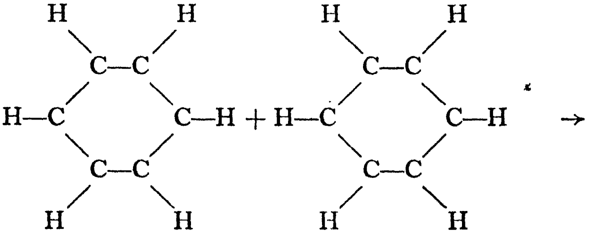
The substance from which we start is acetylene gas—which is easily obtained by the action of water on calcium carbide. Three acetylene molecules, at a fairly high temperature, link together to form benzene. If the benzene is then passed through a red-hot iron tube, two benzene molecules link together to form diphenyl.

The first task of X-ray crystallography, in this field, was to confirm these two general principles of organic chemistry—the tetrahedral carbon bonds and the benzene hexagon. The great difficulty, in finding the structures of organic compounds, is that they are built from atoms with almost the same number of electrons (carbon, oxygen, and nitrogen) which scatter X-rays almost equally. So it is very difficult to locate the positions of the atoms. The pioneer work in this field was done by Debye.

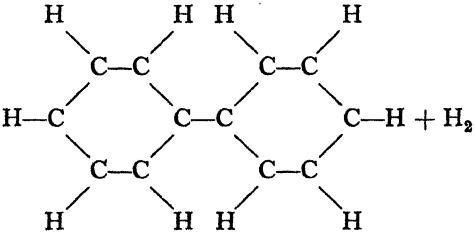
We have already seen, in considering the structure of paraffin wax, that the tetrahedral nature of the carbon bonds would lead to a chain similar to that actually found. Recently the structure of a compound (pentaerythritol), in which four groups are joined to a central carbon atom, has been deter-



3 molecules acetylene → 1 molecule benzene



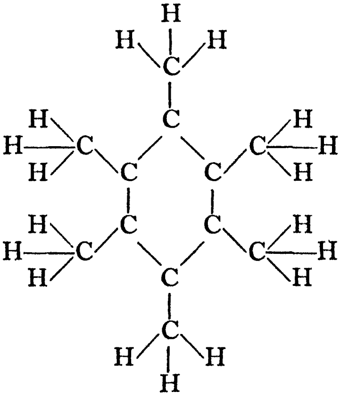
2 molecules benzene →



1 molecule diphenyl + 1 molecule hydrogen

mined. The four groups are each made of one carbon atom, which is linked to an oxygen atom which has also one hydrogen atom joined to it, and also to two hydrogen atoms. The structure fully confirms the tetrahedral nature of the carbon bonds joining these groups to the central carbon atom.

The carbon ring in benzene was shown to be a flat regular hexagon by Mrs. Lonsdale. She actually investigated, for convenience, hexamethyl benzene rather than benzene itself. The structural formula of this compound is given below.



Hexamethyl benzene

The X-ray crystallographer can obtain new results in these investigations which, by the nature of the methods employed, are out of the reach of the organic chemist. X-rays can give us, in addition to the shape of the molecule, its size and the distances between the atoms of which it is composed. In this work of Mrs. Lonsdale, she showed that the distance between two carbon atoms in the benzene ring is 1·42 Å. and between the carbon atom in the side group and the atom to which it is joined in the ring the distance is 1·48 Å.

Each carbon atom in the benzene ring is joined to three other atoms. So, as we saw in the case of graphite, there is one extra electron for each atom, which we cannot specifically assign to a bond. We can regard these " extra " electrons as serving to bind the whole ring more closely together. Thus they fulfil almost the same function as the extra electrons in graphite. In the ordinary tetrahedral bonds, the electrons are serving the same purpose as in diamond. It is, therefore, of interest to compare the distances between carbon atoms in the four cases.*

CARBON-CARBON DISTANCES

Diamond,	1·54 Å.	Long-chain hydrocarbon,	1·534 Å.
Graphite,	1·42 Å.	Benzene ring (actually from anthracene and naphthalene),	1·41 Å.

The results we have so far considered, with the exception of paraffin wax, refer to " complete " structure analyses, that is to say analyses in which the positions of all the atoms are fixed by X-ray methods. It is, however, possible to derive a great deal of information about molecules without performing the laborious task of locating every atom. We have seen that crystals are built by the repetition of a unit block which we have called the unit cell. X-ray analysis gives us comparatively easily the size of these blocks and the symmetry of the various points in the block. The molecules must fit into these blocks, and so any structure of the molecule suggested by the organic chemist can be tested by examining whether molecules with this structure can be fitted into the unit block. In addition, if the centre of the molecule has to be placed on a symmetry element in the block (a centre of symmetry or diad axis, &c.), then the molecule itself must have the same symmetry. Using these methods, it is possible to obtain a considerable amount of information about the structure of the molecule, by means of a short X-ray investigation.

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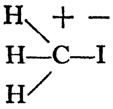
* These figures are taken from J. Monteath Robertson, *Atomic Distances in Organic Compounds by X-ray Analysis*, International Conference on Physics, London, 1934.

The physical properties of the crystal—refractive indices, magnetic properties, &c.—can be used to assist in finding the direction in which the molecule lies. This " surveying " kind of X-ray work has been developed mostly by J. D. Bernal, and is now being used to elucidate the complex structures of hormones and proteins.

Molecular crystals are built from the molecules we have been considering, by packing them together in the most economical way. The binding between the molecules is largely the result of residual forces (p. 39). The chief interest in molecular crystals in the past has been the structure of the molecule, rather than the way the molecules are packed together. It is only because we have, in order to find the molecular structure, to find the packing, that so much is known about it. There are, however, indications that the way the molecules pack together may be of considerable physical interest in the future.

We saw, in the case of ionic crystals, that we could find what structures were the most stable, by a complicated calculation of the energy in a crystal (p. 70). Recently Müller has been able to calculate the binding energy of a crystal made from long-chain hydrocarbons. This gives a new physical interest to the question of how molecules are packed together, and it is probable that this field will be developed to explain why the various packings occur.

Before leaving the subject of the varieties of patterns and forces in crystals, we will briefly consider a type of force which we have not so far discussed. This is the force between what are called " dipoles ". If we have a molecule which is, as a whole, electrically neutral, then it sometimes happens that one or more links are not perfectly homopolar. The electrons which make up the link, instead of being evenly shared between two atoms, spend more time in the neighbourhood of one atom. The result of this is that we have an excess negative charge on one atom and a deficit on the other, though since these are equal the neutrality of the bond as a whole is not affected. In the molecule of methyl iodide, in which a carbon atom is linked to three hydrogen atoms and one iodine atom, the iodine atom has a small negative charge, and the methyl group (carbon and the three hydrogen atoms) has a small equal positive charge. Such a pair of equal and opposite charges is called a " dipole ". We may represent this diagrammatically.



Methyl iodide

This is what we may call the first step on the ladder to forming an ionic compound, in which an electron is transferred completely from one atom to another. The dipoles exert forces on each other and can influence the crystal structure, even, as in the case of ice, completely determining it.

A molecule of water or ice is made up of one atom of oxygen and two atoms of hydrogen. The two positive hydrogen nuclei, which have each a charge of one unit, are embedded in the electrons surrounding the oxygen nucleus, so that their charge is partially neutralized. Their effective charge, as far as nearby molecules are concerned, is reduced to half a unit, and these charges are located (p. 37) at two corners of a tetrahedron. Since the molecule of water as a whole is electrically neutral, we must have an excess of negative charge at some point, and the electrons are so arranged that there are, effectively, two negative charges of half a unit at the other two corners of the tetrahedron. Let us now consider a single water molecule, surrounded by other water molecules. The positive charges at two positions in the molecule will attract the negative charges in neighbouring molecules, so we shall have two molecules attached at these points by electrical forces. Similarly, at the other two points which are negatively charged, two more molecules will be attached, in this case by means of the points in them which are positively charged. Thus each molecule has four neighbours arranged tetrahedrally (fig. 52), the main attraction between the molecules being the electrical forces between the centres of positive and negative electricity.

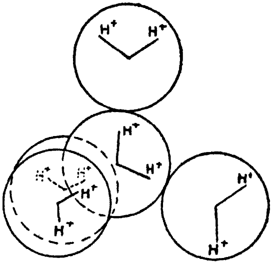


Fig. 52.—Co-ordination of Water Molecules

In both ice and water each molecule has four neighbours, but in ice this leads to a very open type of structure. In water the more violent molecular motion has collapsed the open structure, though retaining the fundamental fourfold co-ordination. This explains the decrease in volume of ice on melting, and the expansion which takes place when water freezes. The structural change is the basic root of all burst drain pipes and boilers, when water freezes inside them. As water is warmed from the freezing-point a further collapse occurs until 4° C. is reached—the point of maximum density—after which the increased disorder and violence of motion of the molecules causes an expansion to take place.

Twenty years have seen marvellous achievements in finding the arrangements of the atoms in solids. The next twenty years will see further advances—in particular into the field of life itself. Organization in crystals and organization in life may well be of the same nature. Only with the increased complication of arrangement in living substances, new possibilities arise, permitting variations in function and new types of change. It is through the discovery of arrangement and order that the direct attack on the problems of living organisms can be made. This type of work is now being carried a stage further by the investigations of J. D. Bernal into the nature of the virus which causes the tobacco mosaic disease. The virus stands very near to the borderline between living and dead matter, and the results already obtained show how profitable the direct investigation of structure made possible by the use of X-rays will be in future years in this field.

CHAPTER XII

The Physical Properties of Crystals

> " Owing to the new methods of crystal analysis the centre of interest has changed. The new methods probe deeply into the crystal structure, telling us how the atoms are arranged, and throwing light on the nature of the molecule and the relation between structure and physical properties. If they had been available at the outset, it is probable that the study of external crystal form would have received comparatively little attention. Historically, this study has been of vital importance, as one of the few indications of the underlying structure. The analysis of crystal symmetry was inspired by it, and all the formal apparatus was prepared long before it could be fully applied to actual atomic arrangements. Our views are still coloured by this historical development."
> —SIR W. H. BRAGG and W. L. BRAGG, *The Crystalline State.*

Throughout the chapters in which we have described the various types of crystal structures, we have included short accounts of the relation between the atomic arrangement and the physical properties of the crystal. In the present chapter, we shall try to outline the general principles governing the relation of the crystal structure to the physical properties of the crystal.

The physical properties of a crystal can be divided into three classes, in which the crystal structure plays essentially different rôles. These are: (1) properties depending solely on the atoms of which the crystal is built, and not on their arrangement; (2) properties directly determined by the nature and arrangement of the atoms; (3) properties in which the method of growth of the crystals, their past history, and the condition of the surface play a fundamental part. As we go from (1) to (3) we introduce at each stage a new factor; (1) depends on the atoms only, (2) involves the arrangement as well, and (3) requires a consideration of the large-scale construction, imperfections, &c.

1. Properties depending solely on the Atoms.

Since these properties depend solely on the atoms, they must be concerned with parts of the atom which are unaffected by the presence or absence of neighbouring atoms. It is evident that all changes which involve the nucleus fulfil this condition, since the energy of chemical combination between two atoms is infinitesimal compared with the energy necessary to produce a change in the nucleus. So all the properties which result in the breakdown of the nucleus, either of its own initiative, as in radioactive change, or by bombardment, as in artificial disintegrations, are dependent only on the atoms present in the crystal.

In addition to those properties concerned only with the nucleus, we can include here the properties which are connected with changes in the inner electrons. These electrons, as we saw in Chapter IV, are left unaffected by the chemical changes when atoms combine, so that properties mainly concerning them are left unchanged by the atom being in a crystal. The absorption of X-rays is one of the more important of these properties.

2. Properties depending on the Arrangement.

A large proportion of the properties of crystals—crystalline form, cleavage, hardness, gliding, certain elastic properties, expansion on heating, specific heats, optical properties, &c.—are included in this class. In certain cases, complete calculations can be made of these properties from the knowledge we have of the nature of the atom, and from the atomic arrangement. We will note here one or two empirical rules which are very useful, and which are also largely confirmed by more extensive theories.

The energy involved in making a crystal face is least when this face is most closely packed with atoms. An atom inside the crystal has less energy than when it is outside, since otherwise a crystal would fly apart. So the more completely an atom is surrounded by other atoms, the lower its energy will be. Possible faces of the crystal will, therefore, have least energy when the atoms in them are most completely surrounded by other atoms, i.e. when the face is one in which the atoms are very densely packed.

This rule has three consequences. Firstly, all crystal faces must go through a number of lattice points, in order that there may be a considerable density of atoms in the faces. This gives us the relation of the faces, considered as packed with atoms, to the faces we obtained in Chapter II by removing blocks, since the corners of these blocks can be taken to be the lattice points. Secondly, faces which go through neighbouring lattice points will be more densely packed than those with large gaps between the lattice points. So faces with low indices will be those most likely to occur. Thirdly, of those faces with low indices, those most densely packed with atoms will be found in the crystal. Common salt may be taken as an example of this, since the densely packed cubic planes in the crystal structure actually form the crystal faces. This last rule is by no means universally applicable, since the crystal faces developed depend so extensively on the conditions of growth, but it furnishes a general guide.

Cleavage planes in a crystal are those planes across which binding is weakest. On inserting a knife edge into the crystal, the cleavage occurs so that the least number of bonds have to be broken. This is beautifully illustrated by graphite (fig. 48). The weak binding between the sheets of atoms makes cleavage very easy parallel to the sheets, but it is very difficult to break the flakes formed by this cleavage in the other directions. Quartz shows how the rule applies when there is no cleavage. In quartz we have a very even distribution of bonds in all directions, so that there is no plane across which the binding is weak. So quartz does not cleave, but fractures when split.

We have already considered (p. 59) the relation of gliding to the atomic arrangement.

Hardness depends on the strength of binding in the crystal, as do also the elastic properties (ability to resist bending, twisting, or being pulled out). Thus diamond is very hard, common salt is fairly hard, and paraffin wax is very soft, corresponding to the strength of binding.

We shall not consider the other properties in detail. We may, however, say that the symmetry of the atomic arrangement gives symmetry to these physical properties. Thus the high symmetry of common salt results in the optical properties, for instance, being the same no matter which direction is used in their measurement, whereas in calcite there is an appreciable difference with direction (p. 77).

3. Properties depending on Growth, &c.

The most striking of these properties is " strength ". The strength of a crystal is the force, per unit area of cross-section, required to break it. If we take a rod of common salt and hang weights on it, then a certain minimum weight will break it. Evidently the greater the thickness the larger this weight would have to be, so we take the weight divided by the area of a section across the rod, as a measure of the " strength ". We can calculate, for a perfect crystal of sodium chloride, what this strength should be. It is 200 Kgm. per square millimetre, but the measured strength is only about 0·5 Kgm. per square millimetre. Joffé, working in Leningrad, showed that, if the crystal is pulled out while its surface is being dissolved, the strength is greatly increased, and so it appears that the presence of small cracks in the surface have a critical effect on the strength of crystals.

Many other properties show a great range of variation, depending on the method of growth of the crystal and its subsequent treatment. Various theories of periodic irregularities, cracks, small blocks, &c., have been brought forward to explain these properties, but the subject is still open and awaits further exhaustive experimental work.

There is a tendency to-day to regard the frontiers of science as so far removed that years must be spent going over the intermediate territory before a glimpse of the new fields is obtained. This is largely the result of a method of teaching which uses a traditional development of the subject, without any insight into the historical process by which science develops. In X-ray crystallography, the subject is so new that, even at a first acquaintance, we meet at every turn new fields awaiting development. The achievements of the past are merely a point of departure for ever fresh triumphs in our knowledge of, and mastery over, all the complex arrangements of atoms which make up every material object.

APPENDIX I

Bibliography

The books in this bibliography are divided into three classes: (1) Elementary, which are roughly of the same standard of difficulty as this volume. (2) Moderate, which are comprehensible to those with a general knowledge of physics and chemistry. (3) Advanced, which are specifically for those most interested in crystallography. In a class by itself is the volume *The Crystalline State*, by Sir W. H. Bragg and W. L. Bragg, which is an extensive survey of the whole field. The list is not exhaustive—only the more important works being included.

Elementary.

A. E. H. Tutton, *Crystals.* Classical crystallography and the optical properties of crystals.

T. V. Barker, *The Study of Crystals.* Especially suitable to those who wish to do experimental work with little apparatus.

Sir W. H. Bragg, *An Introduction to Crystal Analysis.* The methods of structure analysis.

Moderate.

R. O. Hassel and R. C. Evans, *Crystal Chemistry.* A short survey of crystal chemistry.

W. Hume-Rothery, *The Structure of Metals and Alloys.* A clear exposition of the problems of the metallic state.

W. L. Bragg, *The Structure of the Silicates.*

Advanced.

A. F. Joffé, *The Physics of Crystals.* The mechanical and electrical properties of crystals.

R. W. G. Wyckoff, *The Structure of Crystals.* Methods of analysis and all structures up to 1930.

P. P. Ewald and C. Hermann, *Strukturbericht*, 1913–1928. Summary of all structures in this period.

In addition there is a second volume of Wyckoff's book bringing the structures up to 1934, and of the *Strukturbericht* bringing it up to 1932.

APPENDIX II

The Periodic Classification and the Electronic Structure of the Elements

In the Table the electronic structures of the elements are set out, and the elements are arranged in such a way that the close relation of chemical properties to electronic structure is emphasized. After row 3 it is clearer to divide each column into two, for there is little in common between elements of rows 4*A* and 4*B*, which are in the same column. On the other hand the elements in the same column for rows 4*A* and 5*A* resemble each other as do those of rows 4*B* and 5*B* (owing to limitations of space this point could not be clearly brought out in the Table). The Table as it stands is identical in arrangement with that of Mendeléeff in his classical work on the relations between the elements; the modified form which brings out the dissimilarity between 4*A* and 4*B*, &c., was originally suggested on purely chemical grounds by T. Bayley in 1882, but the explanation of it was given by Bohr in 1922.

For each element the Table gives the following particulars:

Symbol of the Element.	Number of positive charges on the nucleus which equals the number of electrons in the neutral atom.
Arrangement of the electrons in the neutral atom. Outer electrons last.	

The following list gives the names and symbols of the elements in order of increasing atomic number.

H	Hydrogen	Ga	Gallium	Il	Illinium
He	Helium	Ge	Germanium	Sm	Samarium
Li	Lithium	As	Arsenic	Eu	Europium
Be	Beryllium	Se	Selenium	Gd	Gadolinium
B	Boron	Br	Bromine	Tb	Terbium
C	Carbon	Kr	Krypton	Dy	Dysprosium
N	Nitrogen	Rb	Rubidium	Ho	Holmium
O	Oxygen	Sr	Strontium	Er	Erbium
F	Fluorine	Y	Yttrium	Tm	Thulium
Ne	Neon	Zr	Zirconium	Yb	Ytterbium
Na	Sodium	Nb	Niobium	Lu	Lutecium
Mg	Magnesium	Mo	Molybdenum	Hf	Hafnium
Al	Aluminium	Ma	Masurium	Ta	Tantalum
Si	Silicon	Ru	Ruthenium	W	Tungsten
P	Phosphorus	Rh	Rhodium	Re	Rhenium
S	Sulphur	Pd	Palladium	Os	Osmium
Cl	Chlorine	Ag	Silver	Ir	Iridium
A	Argon	Cd	Cadmium	Pt	Platinum
K	Potassium	In	Indium	Au	Gold
Ca	Calcium	Sn	Tin	Hg	Mercury
Sc	Scandium	Sb	Antimony	Tl	Thallium
Ti	Titanium	Te	Tellurium	Pb	Lead
V	Vanadium	I	Iodine	Bi	Bismuth
Cr	Chromium	X	Xenon	Po	Polonium
Mn	Manganese	Cs	Cæsium	Rn	Radium Emanation
Fe	Iron	Ba	Barium	Ra	Radium
Co	Cobalt	La	Lanthanum	Ac	Actinium
Ni	Nickel	Ce	Cerium	Th	Thorium
Cu	Copper	Pr	Praseodymium	Pa	Proto-actinium
Zn	Zinc	Nd	Neodymium	U	Uranium
				90.	

APPENDIX III

Apparatus

For the experiments on crystallization it is necessary to have a few fairly large test tubes and some crystallizing dishes. The test tubes can be obtained from a chemist, and the dishes can be obtained from a firm by ordering through a chemist. The dishes obtained with preserved meats (tongues, &c.) can be used provided they are warmed before the hot solution is poured into them. If this precaution is not taken they will crack. The test tubes can be warmed over a gas-stove burner.

Brass wire or rod is better for the cubic framework than copper, since it is more rigid. After some experience has been obtained with the cubic framework other models can be made. In the hexagonal unit of pattern, the sides of the base are equal and the angles in the base are 120° and 60°.

Those wishing to do more experiments are recommended to work from T. V. Barker's book, *The Study of Crystals*, where a full list of the necessary apparatus is given.

APPENDIX IV

Notes on the Elements

These are a few notes on some of the less well-known elements to which reference has been made in this book. All of them can be seen in the Science Museum, South Kensington.

Arsenic, As. Steel-grey, semi-metallic substance. " White arsenic " is the oxide of arsenic.

Bismuth, Bi. Greyish white solid. Hard and brittle. Bad conductor of electricity.

Bromine, Br. Heavy, deep red liquid. Reacts with metals to give bromides.

Cæsium, Cs. Soft, light metal. Reacts with water, chlorine, &c., violently.

Calcium, Ca. Soft metal. Less reactive than sodium.

Chlorine, Cl. Heavy, greenish yellow gas. Reacts with metals to give chlorides.

Fluorine, F. Light, yellow gas. Violently reactive, giving fluorides with metals.

Iodine, I. Dark violet crystalline solid. Least reactive of the four halogens, fluorine, chlorine, bromine and iodine.

Lithium, Li. Soft, light metal. Less reactive than sodium.

Phosphorus, P. Can be obtained in two forms " red " and " yellow ".

Potassium, K. Soft, light metal. More reactive than sodium but less so than cæsium.

Selenium, Se. Red-brown solid. Electrical conductivity depends on exposure to light.

Silicon, Si. Dark grey crystalline solid. Fairly hard.

Sodium, Na. Soft, light metal. Very reactive.

INDEX

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